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APPLICATION NO.	FILING DATE	FIRST NAMED INVENTOR	ATTORNEY DOCKET NO.	CONFIRMATION NO.
10/506,896	09/07/2004	Hiroaki Tatematsu	HEIW:034	5425

6160 7590 07/22/2005

PARKHURST & WENDEL, L.L.P.
1421 PRINCE STREET
SUITE 210
ALEXANDRIA, VA 22314-2805

EXAMINER	
ZEMEL, IRINA SOPJIA	
ART UNIT	**PAPER NUMBER**
1711	

DATE MAILED: 07/22/2005

Please find below and/or attached an Office communication concerning this application or proceeding.

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PTO-90C (Rev. 10/03)

Office Action Summary	Application No. 10/506,896	Applicant(s) TATEMATSU ET AL.	
	Examiner Irina S. Zemel	Art Unit 1711	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

Period for Reply

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If the period for reply specified above is less than thirty (30) days, a reply within the statutory minimum of thirty (30) days will be considered timely.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

Status

1)☒ Responsive to communication(s) filed on *07 September 2004*.

2a)☐ This action is **FINAL**. 2b)☒ This action is non-final.

3)☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

Disposition of Claims

4)☒ Claim(s) *1-6* is/are pending in the application.

4a) Of the above claim(s) _____ is/are withdrawn from consideration.

5)☐ Claim(s) _____ is/are allowed.

6)☒ Claim(s) *1-6* is/are rejected.

7)☐ Claim(s) _____ is/are objected to.

8)☐ Claim(s) _____ are subject to restriction and/or election requirement.

Application Papers

9)☐ The specification is objected to by the Examiner.

10)☐ The drawing(s) filed on _____ is/are: a)☐ accepted or b)☐ objected to by the Examiner.

Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).

Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).

11)☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

Priority under 35 U.S.C. § 119

12)☒ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).

a)☒ All b)☐ Some * c)☐ None of:

1.☐ Certified copies of the priority documents have been received.

2.☐ Certified copies of the priority documents have been received in Application No. _____.

3.☒ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

* See the attached detailed Office action for a list of the certified copies not received.

Attachment(s)

1) ☒ Notice of References Cited (PTO-892)

2) ☐ Notice of Draftsperson's Patent Drawing Review (PTO-948)

3) ☒ Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08) Paper No(s)/Mail Date *9-7-2004*.

4) ☐ Interview Summary (PTO-413) Paper No(s)/Mail Date. _____ .

5) ☐ Notice of Informal Patent Application (PTO-152)

6) ☐ Other: _____.

5.0.0

DETAILED ACTION

Claim Objections

Claim 2 is objected to under 37 CFR 1.75(c), as being of improper dependent form for failing to further limit the subject matter of a previous claim. Applicant is required to cancel the claim(s), or amend the claim(s) to place the claim(s) in proper dependent form, or rewrite the claim(s) in independent form. The limitation "preferably" does not actually limit the claims to the specifically recited value or characteristic, and, thus, does not further limit claims 1.

Claim Rejections - 35 USC § 102

The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

> A person shall be entitled to a patent unless –
>
> (a) the invention was known or used by others in this country, or patented or described in a printed publication in this or a foreign country, before the invention thereof by the applicant for a patent.
>
> (b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.
>
> (e) the invention was described in a patent granted on an application for patent by another filed in the United States before the invention thereof by the applicant for patent, or on an international application by another who has fulfilled the requirements of paragraphs (1), (2), and (4) of section 371(c) of this title before the invention thereof by the applicant for patent.

The changes made to 35 U.S.C. 102(e) by the American Inventors Protection Act of 1999 (AIPA) and the Intellectual Property and High Technology Technical Amendments Act of 2002 do not apply when the reference is a U.S. patent resulting directly or indirectly from an international application filed before November 29, 2000. Therefore, the prior art date of the reference is determined under 35 U.S.C. 102(e) prior to the amendment by the AIPA (pre-AIPA 35 U.S.C. 102(e)).

The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

> (a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made.

Claims 1-6 are rejected under 35 U.S.C. 102(e) as anticipated by or, in the alternative, under 35 U.S.C. 103(a) as obvious over JP 2003-49017 to Toray Ind. Inc., (hereinafter "Toray").

Toray discloses polyphenylene sulfide based foamed molded products which are suitable for optical parts and which are obtained by injection molding pf PPS saturated with supercritical carbondioxide. The reference further contemplates addition various inorganic and fibrous fillers (as per claim 3) and addition other polymers that can act as melt tension modifiers.

The reference does not added the relative density of the resulting foams, however, since the compositions are substantially identical to the claimed compositions and are obtained by the methods substantially identical to the methods disclosed in the instant application, it is reasonable believed that the claimed properties are inherently exhibited by the disclosed materials. The burden is shifted to the applicants to provide factual evidence to the contrary.

In respect to limitations of claims 2, (a) – similar inherency argument applies, and (b) – as discussed above, the claim does not actually recite any required limitation since limitation reciting "preferably" is not mandatory.

Claims 1-5 are rejected under 35 U.S.C. 102(e or a) as anticipated by or, in the alternative, under 35 U.S.C. 103(a) as obvious over WO 02/090085 to Trexel, Inc., (hereinafter "Trexel").

Trexel discloses injection molding of microcellular polymeric foams by saturating polymeric materials with supercritical gas (CO2 or nitrogen). Among suitable polymers, polycarbonates and polyesters such as polyethylene terephtalates are disclosed on page 22. The reference further discloses addition of various additives including fillers and other additives which can act as viscosity modifiers. The reference further discloses a foamed and unfoamed articles of the same volume and the weight difference of about 10 %, which, by implication, satisfies the claimed relative density characteristic. See table on page 22. The preamble limitations "for use as optical base" is given weight only to the extent that the composition disclosed in the reference is capable of being used such. The disclosed composition is inherently capable for the claimed use because the claimed composition is believed to be identical to the composition disclosed in the reference. Therefore, the preamble limitation is anticipated by the reference. The burden is shifted to the applicant to provide convincing factual evidence to the contrary.

Claims 1-5 are rejected under 35 U.S.C. 102(a or e) as anticipated by or, in the alternative, under 35 U.S.C. 103(a) as obvious over US patent 6,403,663 to DeSimone et al., (hereinafter "DeSimone").

DeSimone discloses method of making foamed polymeric articles using supercritical carbon dioxide. See, for example, Injection Molding section in columns 7-

8. Suitable polymers disclosed in column 3 and suitable additives disclosed in column 4 fully correspond to the limitations recited in claims 3-5. Once again, the reference does not address the reference does not added the relative density of the resulting foams, however, since the compositions are substantially identical to the claimed compositions and are obtained by the methods substantially identical to the methods disclosed in the instant application, it is reasonable believed that the claimed properties are inherently exhibited by the disclosed materials. The burden is shifted to the applicants to provide factual evidence to the contrary. Also, the preamble limitations "for use as optical base" is given weight only to the extent that the composition disclosed in the reference is capable of being used such. The disclosed composition is inherently capable for the claimed use because the claimed composition is believed to be identical to the composition disclosed in the reference. Therefore, the preamble limitation is anticipated by the reference. The burden is shifted to the applicant to provide convincing factual evidence to the contrary.

Claims 1-3 are rejected under 35 U.S.C. 102(b) as anticipated by or, in the alternative, under 35 U.S.C. 103(a) as obvious over US Patent 5,158,986 to Cha et al., (hereinafter "Cha").

Cha disclosed method of making foamed polymeric articles using supercritical carbon dioxide. See, for example, description of figure 18. Suitable polymers include polycarbonates as per column 6, line 61.

Once again, the reference does not address the reference does not added the relative density of the resulting foams, however, since the compositions are

substantially identical to the claimed compositions and are obtained by the methods substantially identical to the methods disclosed in the instant application, it is reasonable believed that the claimed properties are inherently exhibited by the disclosed materials. The burden is shifted to the applicants to provide factual evidence to the contrary. Also, the preamble limitations "for use as optical base" is given weight only to the extent that the composition disclosed in the reference is capable of being used such. The disclosed composition is inherently capable for the claimed use because the claimed composition is believed to be identical to the composition disclosed in the reference. Therefore, the preamble limitation is anticipated by the reference. The burden is shifted to the applicant to provide convincing factual evidence to the contrary.

Claim Rejections - 35 USC § 103

Claim 6 is rejected under 35 U.S.C. 103(a) as being unpatentable over Trexel in combination with JP62-50801 to Teijin Chem., (hereinafter "Teijin").

The disclosure of Trexel is discussed above. The reference expressly states that molded articles of ANY type can be produced by the methods of the invention, and specifically lists, for example, polycarbonates as suitable polymers. It is well known in the art that foamed polycarbonated are conventionally used for production of molded optical articles as those dclaimed in claim 6. See, for example, Teilin. Therefore, producing a specifically claimed optical articles from compositions disclosed by Trexel

and by the method of Trexel would have been obvious with reasonable expectation of adequate results.

Claim 4-6 are rejected under 35 U.S.C. 103(a) as being unpatentable over Cha in combination with Teijin.

The disclosure of Cha is discussed above. Cha does not expressly disclosed what king of moldings can be obtained by the disclosed method, but, as discussed above, expressly disclosed polycarbonates as suitable materials to produce foamed moldings. It is well known, as discussed above, in the art that foamed polycarbonated are conventionally used for production of molded optical articles as those dclaimed in claim 6. See, for example, Teilin. Therefore, producing a specifically claimed optical articles from compositions disclosed by Trexel and by the method of Trexel would have been obvious with reasonable expectation of adequate results. It is also notoriously known to add various fillers and additives to polycarbonate molding to improve its desired properties (also as contemplated, for example, by Teijin). Thus, invention as claimed would have been obvious from the combined teachings of the above cited references.

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Irina S. Zemel whose telephone number is (571)272-0577. The examiner can normally be reached on Monday-Friday 9-5.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, James Seidleck can be reached on (571)272-1078. The fax phone number for the organization where this application or proceeding is assigned is 703-872-9306.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see http://pair-direct.uspto.gov. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

Irina S. Zemel
Examiner
Art Unit 1711

Irina Zemel

ISZ

DT04 Rec'd PCT/PTO 0 7 SEP 2004

Sheet 1 of 1 FORM PTO 1449 (*modified*) U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE LIST OF REFERENCES CITED BY APPLICANT(S) (*Use several sheets if necessary*)	ATTY DOCKET NO. HEIW:034	SERIAL NO. 10/506896 New Application
	APPLICANT Hiroaki TATEMATSU et al.	
	FILING DATE September 7, 2004	GROUP

U.S. PATENT DOCUMENTS

*EXAMINER INITIAL	DOCUMENT NUMBER	DATE	NAME	CLASS	SUBCLASS	FILING DATE IF APPROPRIATE

FOREIGN PATENT DOCUMENTS

	DOCUMENT NUMBER	DATE	COUNTRY	CLASS	SUBCLASS	TRANSLATION NO	TRANSLATION YES
JJ	2002-363326	12/18/02	Japan (w/English Abstract)			X	abs
JJ	2003-34732	2/7/03	Japan (w/English Abstract)			X	abs
JJ	2001-277280	10/9/01	Japan (w/English Abstract)			X	abs
JJ	2003-89727	3/28/03	Japan (w/English Abstract)			X	abs
JJ	2003-49017	2/21/03	Japan (w/English Abstract)			X	abs

OTHER DOCUMENT(S) (*Including Author, Title, Date, Pertinent Pages, Etc.*)

EXAMINER Ana Fernel	DATE CONSIDERED 7-15-05

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant

Notice of References Cited	Application/Control No. 10/506,896	Applicant(s)/Patent Under Reexamination TATEMATSU ET AL.	
	Examiner Irina S. Zemel	Art Unit 1711	Page 1 of 1

U.S. PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
	A	US-6,403,663	06-2002	DeSimone et al.	521/97
	B	US-5,158,986	10-1992	Cha et al.	521/82
	C	US-			
	D	US-			
	E	US-			
	F	US-			
	G	US-			
	H	US-			
	I	US-			
	J	US-			
	K	US-			
	L	US-			
	M	US-			

FOREIGN PATENT DOCUMENTS

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	Classification
	N	JP2003-770931	02-2003	Japan	Toray Ind.	
	O	JP62-50801	08-1985	Japan	Teijin Chem	
	P	WO02/090085	11-2002	WO	Trexel Inc	
	Q					
	R					
	S					
	T					

NON-PATENT DOCUMENTS

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	
	V	
	W	
	X	

*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

DERWENT-ACC-NO: 2003-770931

DERWENT-WEEK: 200373

TITLE: Polyphenylene sulfide resin foam molded product for electronic components, is obtained by **molding supercritical** fluid and polyphenylene sulfide resin having specific natural logarithmic value of melt index

PATENT-ASSIGNEE: TORAY IND INC[TORA]

PRIORITY-DATA: 2001JP-0242048 (August 9, 2001)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
JP 2003049017 A	February 21, 2003	N/A	012	C08J 009/12

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP2003049017A	N/A	2001JP-0242048	August 9, 2001

INT-CL (IPC): B29C045/00, B29K081:00 , B29K105:04 , B29K105:16 , C08J009/12 , C08L081:02

ABSTRACTED-PUB-NO: JP2003049017A

BASIC-ABSTRACT:

NOVELTY - A polyphenylene sulfide (PPS) resin foam molded product is obtained by injection **molding** a PPS resin and a **supercritical** fluid. The PPS resin has natural logarithmic value of melt index of 3.8-8.8 g/10 minutes.

USE - For optical instruments such as camera, microscope and binocular; precision-instrument related components; machine related components; pump components such as pipe joint; building components; furniture

components;
electrical and electronic components such as sensor, LED lamps and resistors;
television components such as parabolic antenna; computer related components;
microwave oven components; and components for cooling fan, radiator tank,
gasoline chamber and steering horn pad.

ADVANTAGE - The polyphenylene sulfide resin foam molded product has fine and
uniform foam state, without impairing inherent properties of the resin. The
molded product has reduced weight and excellent dimensional accuracy.

CHOSEN-DRAWING: Dwg.0/1

TITLE-TERMS: POLYPHENYLENE SULPHIDE RESIN FOAM MOULD PRODUCT ELECTRONIC
COMPONENT OBTAIN MOULD SUPERCRITICAL FLUID POLYPHENYLENE SULPHIDE
RESIN SPECIFIC NATURAL LOGARITHM VALUE MELT INDEX

DERWENT-CLASS: A26 A32 A95

CPI-CODES: A05-J05A; A08-R; A08-R03A; A08-R04; A11-B06C; A12-S04B; A12-S04C;
A12-S04D; A12-S04E;

ENHANCED-POLYMER-INDEXING:
Polymer Index [1.1]
018 ; D19 D18 D31 D76 D50 D86 ; P1478 P1467 H0293 F00 D01 D18 ;
S9999 S1309*R ; S9999 S1434 ; K9449
Polymer Index [1.2]
018 ; ND07 ; N9999 N6484*R N6440 ; N9999 N6086 ; B9999 B3601 B3554
; K9449 ; Q9999 Q8264*R ; Q9999 Q8286*R Q8264 ; Q9999 Q8355 Q8264
; Q9999 Q7976 Q7885 ; Q9999 Q8719*R ; Q9999 Q6826*R ; Q9999 Q7716
Q7681 ; Q9999 Q7330*R ; Q9999 Q7512 ; Q9999 Q7487 Q7330 ; K9881
K9347 K9790 ; Q9999 Q7705 Q7681 ; Q9999 Q7885*R ; Q9999 Q8480 Q8399
Q8366 ; Q9999 Q9289 Q9212 ; B9999 B4842 B4831 B4740 ; B9999 B3758*R
B3747
Polymer Index [1.3]
018 ; G2891 D00 Si 4A ; R05086 D00 D09 C* 4A ; A999 A237 ; A999
A771 ; S9999 S1070*R
Polymer Index [1.4]
018 ; R01278 D00 F44 C* 4A O* 6A Ca 2A ; A999 A237 ; A999 A771

SECONDARY-ACC-NO:
CPI Secondary Accession Numbers: C2003-211983

(19)日本国特許庁（ＪＰ）　(12)公開特許公報（Ａ）　(11)特許出願公開番号
特開2003－49017
（P2003－49017A）
(43)公開日　平成15年2月21日(2003.2.21)

(51)Int.Cl.⁷	識別記号	ＦＩ	テーマコード゛(参考)
Ｃ０８Ｊ　9/12	ＣＥＺ	Ｃ０８Ｊ　9/12	ＣＥＺ　４Ｆ０７４
Ｂ２９Ｃ　45/00		Ｂ２９Ｃ　45/00	４Ｆ２０６
// Ｂ２９Ｋ　81:00		Ｂ２９Ｋ　81:00	
105:04		105:04	
105:16		105:16	

審査請求　未請求　請求項の数３　ＯＬ　（全12頁）　最終頁に続く

(21)出願番号　特願2001－242048(P2001－242048)

(22)出願日　平成13年8月9日(2001.8.9)

(71)出願人　000003159
東レ株式会社
東京都中央区日本橋室町２丁目２番１号

(72)発明者　沖田　茂
東京都中央区日本橋室町２丁目２番１号
東レ株式会社東京事業場内

Ｆターム(参考)　4F074 AA87 AC02 AC26 AC34 AE04 AG02 AG06 AG07 AG10 AG11 BA08 BA32 BA33 CA26 CB91 DA03 DA08
4F206 AA34 AB02 AB11 AB16 AB25 AG20 JA04 JF02 JF04

(54)【発明の名称】　ポリフェニレンスルフィド樹脂発泡成形品

(57)【要約】
【課題】　ポリフェニレンスルフィド樹脂本来の特性を損なわずに微細かつ均一な発泡状態を有するポリフェニレンスルフィド樹脂発泡成形品の提供。
【解決手段】　ポリフェニレンスルフィド樹脂と超臨界流体とを射出成形機に導入し、射出成形して得られるポリフェニレンスルフィド樹脂発泡成形品であって、前記ポリフェニレンスルフィド樹脂のメルトインデックスの自然対数値が３．８～８．８であることを特徴とする。

1

【特許請求の範囲】

【請求項１】　ポリフェニレンスルフィド樹脂と超臨界流体とを射出成形機に導入し、射出成形して得られるポリフェニレンスルフィド樹脂発泡成形品であって、前記ポリフェニレンスルフィド樹脂のメルトインデックス（ｇ／１０ｍｉｎ）の自然対数値が３．８～８．８であることを特徴とするポリフェニレンスルフィド樹脂発泡成形品。

【請求項２】　前記ポリフェニレンスルフィド樹脂が、無機充填材を含有することを特徴とする請求項１記載のポリフェニレンスルフィド樹脂発泡成形品。

【請求項３】　前記無機充填材が、ガラス繊維、炭酸カルシウムおよび炭素繊維から選ばれた１種以上であることを特徴とする請求項２記載のポリフェニレンスルフィド樹脂発泡成形品。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、ポリフェニレンスルフィド樹脂本来の特性を損なわずに微細かつ均一な発泡状態を有するポリフェニレンスルフィド樹脂発泡成形品に関するものである。

【０００２】

【従来の技術】ポリフェニレンスルフィド樹脂は、優れた成形性、機械特性、耐熱性、耐久性および耐薬品性などを有していることから、これらの特性を生かして自動車用途や電気・電子用途を始めとする種々の用途に広く利用されている。そして、ポリフェニレンスルフィド樹脂は、特に金属に比べて比重が小さいため、軽量化の目的で金属代替用途に使用されるケースが多いが、近年では更なる軽量化の要望が強い。

【０００３】しかしながら、ポリフェニレンスルフィド樹脂を用いて均一かつ微細な発泡状態を有する発泡成形品を製造する方法については現状では知られていない。

【０００４】一般に、樹脂発泡成形品を得る方法としては、例えば有機または無機の熱分解性発泡剤による発泡法および揮発性発泡剤による発泡法などが知られており、これらについては、「実用プラスチック成形加工事典」、産業調査会、１９９７年発行、第３９８～４００ページに記載されているが、これらの発泡方法ではポリフェニレンスルフィド樹脂を微細かつ均一に発泡させることが難しく、結果としてポリフェニレンスルフィド樹脂が有する本来の特性が発揮できないという問題があった。

【０００５】一方、近年では、超臨界流体を用いた発泡成形技術の研究開発が盛んに行われており、射出成形機に樹脂と共に超臨界状態の窒素ガスや炭酸ガスを導入して発泡樹脂成形品を得るという射出成形技術が開発されている。

【０００６】例えば、超臨界流体を樹脂材料に連続的に導入して材料を発泡させて得られる発泡体（米国特許第

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４４７３６６５号、米国特許第５１５８９８６号、米国特許５３３４３５６号、日本特許２６２５５７６号）、およびスチレン系樹脂５０～９９重量部とポリプロピレン樹脂１～５０重量部からなる樹脂組成物を射出成形する際に超臨界流体を導入して発泡成形品を得る方法（特開平１０－２４４３６号公報）などが知られている。

【０００７】しかしながら、上記「実用プラスチック成形加工事典」、産業調査会、１９９７年発行、３９８～４００ページに記載されている方法を単純にポリフェニレンスルフィド樹脂に適用したとしても、ポリフェニレンスルフィド樹脂に微細かつ均一な発泡状態を形成させることが難しい場合があり、結果としてポリフェニレンスルフィド樹脂が有する本来の特性が発揮できないという問題があることが判明した。

【０００８】また、上記米国特許第４４７３６６５号、米国特許第５１５８９８６号、米国特許５３３４３５６号、日本特許２６２５５７６号、および上記特開平１０－２４４３６号公報には、超臨界流体を用いた発泡射出成形方法については記載されているものの、ポリフェニレンスルフィド樹脂の発泡に関する記述については全く認められない。

【０００９】このように、ポリフェニレンスルフィド樹脂を用いて、その特性を損なわずに微細かつ均一な発泡状態を有する射出発泡成形品を得る方法はこれまで見出されていなかった。

【００１０】

【発明が解決しようとする課題】本発明は、上述した従来技術における問題点の解決を課題として検討した結果達成されたものである。

【００１１】したがって、本発明の目的は、ポリフェニレンスルフィド樹脂本来の特性を損なうことなく微細かつ均一な発泡状態を有するポリフェニレンスルフィド樹脂発泡成形品を提供することにある。

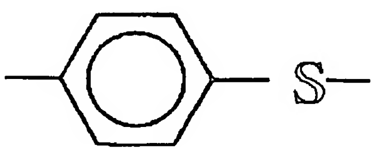
【００１２】

【課題を解決するための手段】本発明らは、上記の課題を解決すべく検討した結果、特定のメルトインデックスを有するポリフェニレンスルフィド樹脂を用い、このポリフェニレンスルフィド樹脂と超臨界流体とを射出成形機に導入して射出成形することによって、上記の目的に合致したポリフェニレンスルフィド樹脂発泡成形品が得られることを見出し、本発明に到達した。

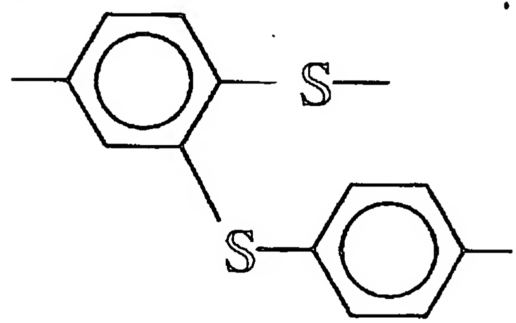
【００１３】すなわち、本発明のポリフェニレンスルフィド樹脂発泡成形品は、ポリフェニレンスルフィド樹脂と超臨界流体とを射出成形機に導入し、射出成形して得られるポリフェニレンスルフィド樹脂発泡成形品であって、前記ポリフェニレンスルフィド樹脂のメルトインデックス（ｇ／１０ｍｉｎ）の自然対数値が３．８～８．８であることを特徴とする。

【００１４】そして、本発明のポリフェニレンスルフィド樹脂発泡成形品においては、前記ポリフェニレンスルフィド樹脂発泡成形品においては、前記ポリフェニレンスルフ

フィド樹脂が無機充填材を含有すること、および前記無機充填材がガラス繊維、炭酸カルシウムおよび炭素繊維から選ばれた1種以上であることが、いずれも好ましい条件である。
【0015】
【発明の実施の形態】以下、本発明のポリフェニレンスルフィド樹脂発泡成形品について詳細に説明する。なお、本発明において「重量」とは「質量」を意味する。
【0016】本発明で用いるポリフェニレンスルフィド樹脂とは、下記一般式（1）で表される繰り返し単位を有する重合体であり、前記繰り返し単位の含有量は、耐熱性の面から70モル％以上であることが好ましく、より好ましくは80モル％以上、特に好ましくは90モル％以上である。前記繰り返し単位の含有量が70モル％未満の場合には、耐熱性および剛性が低下する傾向が見られる。
【0017】
【化1】

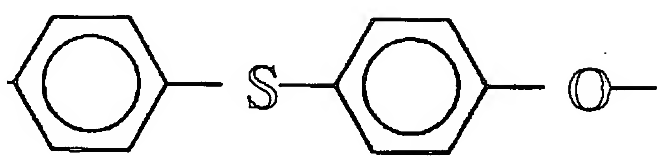


＊【0018】ここで、前記一般式（1）で表される繰り返し単位以外の繰り返し単位としては、下記一般式（2）～（8）で表される構造単位が用いられる。
【0019】
【化2】

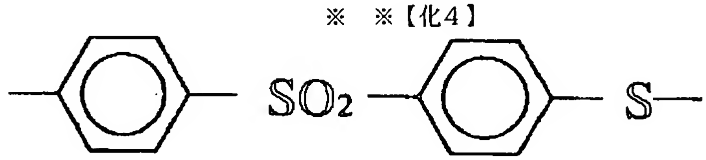


【0020】
【化3】

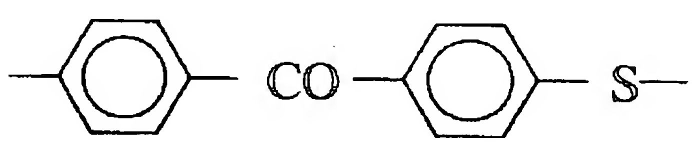
＊



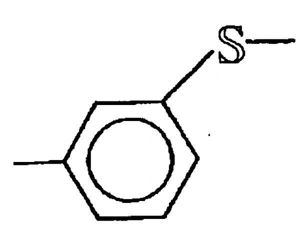
【0021】 ※ ※【化4】



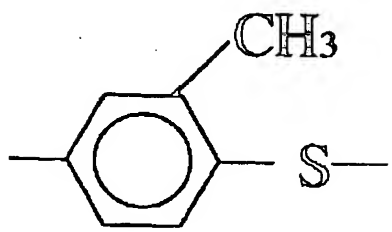
【0022】 ☆ ☆【化5】



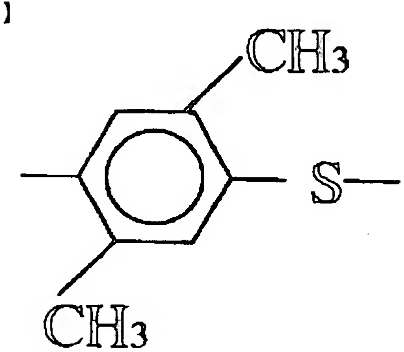
【0023】 ☆
【化6】 ☆



【0024】
【化7】



【0025】
【化8】



【0026】本発明で用いるポリフェニレンスルフィド樹脂は、長さ8mm、ノズル径2．095mmのオリフィスを用い、荷重5kg、温度315．6℃、サンプル量7g、サンプル仕込みから測定開始までのプレヒート時間5minでの条件で測定した時のメルトインデックス（g／10min）の自然対数値が3．8〜8．8、好ましくは4．2〜8．0、更に好ましくは4．6〜7．8の範囲にあることを必須の要件とする。

【0027】ポリフェニレンスルフィド樹脂のメルトインデックスの自然対数値が上記の範囲を外れる場合には、微細かつ均一な発泡状態を形成させることができない。その理由については完全には明らかにされてはいないが、ポリフェニレンスルフィド樹脂と超臨界流体との粘度比およびポリフェニレンスルフィド樹脂末端と超臨界流体との親和性が、超臨界流体の分散性に大きく影響することに起因すると考えられ、メルトインデックスの自然対数値がこれらの因子と強い相関関係を有しているためであると予想される。

【0028】また、本発明で用いるポリフェニレンスルフィド樹脂の灰分は、450〜500℃で炭化させた後、538℃で6時間灰化させた時の灰分残渣量で0．30重量%以下、好ましくは0．25重量%以下、更に好ましくは0．22重量%以下であることが望ましい。

【0029】このようなポリフェニレンスルフィド樹脂は、公知の方法、例えば特公昭45−3368号公報、特公昭52−12240号公報、および特開昭61−7332号公報などに記載されている方法を用いて製造することができる。

【0030】本発明においては、上記公報に記載されている方法で得られたポリフェニレンスルフィド樹脂を、空気中加熱による架橋・高分子量化、窒素などのガス雰囲気下あるいは減圧下での熱処理、および有機溶剤・熱水・酸性水溶液・アルカリ性水溶液などによる洗浄などを施した上で使用してもよい。特に、有機溶剤で洗浄した場合には、低分子量成分が除去されるため、溶融成形時のガス発生、金型腐蝕が低減される。その場合に使用する有機溶剤としては、N−メチルピロリドン、N，N’−ジメチルホルムアミド、N，N’−ジメチルアセトアミド、1，3−ジメチルイミダゾリジノン、ヘキサメチルホスホンアミド、ピペラジノンなどの含窒素溶剤、ジメチルスルホキシド、ジメチルスルホン、スルホランなどのスルホン系溶剤、アセトン、メチルエチルケトン、ジエチルケトン、アセトフェノンなどのケトン系溶剤、ジメチルエーテル、ジエチルエーテル、ジプロピルエーテル、1，4−ジオキサン、テトラヒドロフランなどのエーテル系溶剤、クロロホルム、メチレンジクロリド、四塩化炭素、トリクロロエチレン、ジクロロエチレン、クロルベンゼンなどのハロゲン系溶剤、メタノール、エタノール、プロパノール、ブタノール、ペンタノール、エチレングリコール、プロピレングリコール、ポリエチレングリコール、ポリプロピレングリコールなどのアルコール系溶剤、フェノール、クレゾールなどのフェノール系溶剤、ベンゼン、トルエン、キシレンなどの芳香族炭化水素系溶剤、およびペンタン、ヘキサン、シクロヘキサン、ヘプタン、オクタンなどの飽和炭化水素系溶剤などが挙げられる。

【0031】また、洗浄に用いる酸性水溶液およびアルカリ性水溶液については、ポリフェニレンスルフィド樹脂を分解する作用のないものであれば特に制限はなく、例えば酢酸、塩酸、硫酸、燐酸、有機カルボン酸、有機スルホン酸、および各種水酸化アルカリ水溶液などが用いられる。

【0032】なお、ポリフェニレンスルフィド樹脂を、酸無水物、エポキシ基、イソシアネート基などの官能基を有する化合物で処理してから用いることもできる。

【0033】本発明で使用するポリフェニレンスルフィド樹脂は、無機充填材を含有していてもよい。

【0034】本発明で使用し得る無機充填材としては、一般に強化ポリフェニレンスルフィド樹脂に使用されるガラス繊維、炭酸カルシウムおよび炭素繊維が好ましいが、その他の様々な繊維状または非繊維状の充填材を用いることにより、さらに成形品表面性などの改善を図ることも可能である。ガラス繊維に代表される無機充填材の繊維径および繊維長については特に限定はない。その他の無機充填材の例としては、チタン酸カリウムウィスカ、酸化亜鉛ウィスカ、硼酸アルミニウムウィスカ、アラミド繊維、アルミナ繊維、炭化珪素繊維、セラミック繊維、アスベスト繊維、石コウ繊維、金属繊維などの繊維状充填剤、ワラステナイト、ゼオライト、セリサイ

ト、カオリン、マイカ、クレー、パイロフィライト、ベントナイト、アスベスト、タルク、アルミナシリケートなどの珪酸塩、アルミナ、酸化珪素、酸化マグネシウム、酸化ジルコニウム、酸化チタン、酸化鉄などの金属酸化物、炭酸カルシウム、炭酸マグネシウム、ドロマイトなどの炭酸塩、硫酸カルシウム、硫酸バリウムなどの硫酸塩、水酸化マグネシウム、水酸化カルシウム、水酸化アルミニウムなどの水酸化物、ガラスフレーク、ガラスビーズ、セラミックビーズ、窒化ホウ素、炭化珪素およびシリカなどの非繊維状充填材などが挙げられ、これらは中空であってもよい。これら充填材を複数種類併用することも可能である。 また、これら繊維状／非繊維状の無機充填材を、イソシアネート系化合物、有機シラン系化合物、有機チタネート系化合物、有機ボラン系化合物、およびエポキシ化合物などのカップリング剤で同時にもしくは予備的に処理して使用することは、より優れた機械的特性や成形品外観を得る意味において好ましい。

【００３５】無機充填材の添加量については特に制限はないが、通常はポリフェニレンスルフィド樹脂１００重量部に対して５〜１９００重量部、好ましくはポリフェニレンスルフィド樹脂１００重量部に対して１０〜９００重量部、更に好ましくはポリフェニレンスルフィド樹脂１００重量部に対して２０〜６００重量部の範囲である。

【００３６】さらに、ポリフェニレンスルフィド樹脂には、本発明の目的を損なわない範囲で、要求される特性に応じて、他のポリマー類、添加剤、結晶核剤、耐熱剤や紫外線吸収剤などの安定剤、難燃剤、帯電防止剤、可塑剤、滑剤、着色剤およびカップリング剤などを添加することも可能である。

【００３７】また、本発明で用いられるポリフェニレンスルフィド樹脂に対し、エポキシ基、アミノ基、イソシアネート基、水酸基、メルカプト基およびウレイド基の中から選ばれた少なくとも１種の官能基を有するアルコキシシランを添加することは、機械的強度、靭性などの向上にとって有効である。かかる化合物の具体例としては、γ−グリシドキシプロピルトリメトキシシラン、γ−グリシドキシプロピルトリエトキシシラン、β−（３，４−エポキシシクロヘキシル）エチルトリメトキシシランなどのエポキシ基含有アルコキシシラン化合物、γ−メルカプトプロピルトリメトキシシラン、γ−メルカプトプロピルトリエトキシシランなどのメルカプト基含有アルコキシシラン化合物、γ−ウレイドプロピルトリエトキシシラン、γ−ウレイドプロピルトリメトキシシラン、γ−（２−ウレイドエチル）アミノプロピルトリメトキシシランなどのウレイド基含有アルコキシシラン化合物、γ−イソシアナトプロピルトリエトキシシラン、γ−イソシアナトプロピルトリメトキシシラン、γ−イソシアナトプロピルメチルジメトキシシラン、γ−イソシアナトプロピルメチルジエトキシシラン、γ−イソシアナトプロピルエチルジメトキシシラン、γ−イソシアナトプロピルエチルジエトキシシラン、γ−イソシアナトプロピルトリクロロシランなどのイソシアナト基含有アルコキシシラン化合物、γ−（２−アミノエチル）アミノプロピルメチルジメトキシシラン、γ−（２−アミノエチル）アミノプロピルトリメトキシシラン、γ−アミノプロピルトリメトキシシランなどのアミノ基含有アルコキシシラン化合物、およびγ−ヒドロキシプロピルトリメトキシシラン、γ−ヒドロキシプロピルトリエトキシシランなどの水酸基含有アルコキシシラン化合物などが挙げられる。

【００３８】かかるシラン化合物の好適な添加量は、ポリフェニレンスルフィド樹脂１００重量部に対し、０．０５〜５重量部の範囲が選択される。

【００３９】本発明で使用される超臨界流体としては、射出成形時に超臨界状態となって使用されるものであれば、特に制限はない。超臨界流体は単一物質であっても、混合物であってもかまわない。一般的には、二酸化炭素、窒素、アルゴンおよびヘリウムなどの不活性ガスが使用され、二酸化炭素および窒素が好ましく用いられ、特に好ましくは二酸化炭素である。

【００４０】射出成形時に注入される超臨界流体の量については特に制限はないが、通常はポリフェニレンスルフィド樹脂１００重量部に対して０．０１〜１００重量部、好ましくは０．０５〜５０重量部、更に好ましくは０．１〜３０重量部の範囲である。

【００４１】射出成形中に溶融ポリフェニレンスルフィド樹脂に超臨界流体を注入する方法については特に制限はないが、たとえば、気体状態の不活性ガスをそのまま注入する方法、加圧して注入する方法、減圧して注入する方法、および液体状態または超臨界流体状態の不活性ガスをプランジャーポンプなどにより注入する方法などが挙げられる。

【００４２】次に、本発明のポリフェニレンスルフィド樹脂発泡成形品を製造する方法の一例について、図１の構成概略図を用いて説明する。

【００４３】まず、ポリフェニレンスルフィド樹脂ペレットＡをホッパーＢより供給し、加熱溶融させる。超臨界流体となる窒素や炭酸ガスなどの不活性ガスは、ガスボンベＫより供給され、昇圧ポンプＪによって昇圧された後、溶融したポリフェニレンスルフィド樹脂に供給される。この際、不活性ガスは超臨界流体となって供給されてもよいし、射出成形のシリンダー内に供給されてから超臨界流体になってもかまわない。シリンダーＤの内部は、供給された不活性ガスが超臨界状態を保ち、溶融したポリフェニレンスルフィド樹脂内に短時間で溶解・拡散されるように、臨界温度以上かつ臨界圧力以上に保たれている。例えば、窒素の場合、臨界温度は−１２７℃、臨界圧力は３．５ＭＰａであり、炭酸ガスの場合、

臨界温度は31℃、臨界圧力は7．4MPaである。
【0044】シリンダーD内にて溶融ポリフェニレンスルフィド樹脂と不活性ガスがスクリューCによって混練され、更にスタティックミキサーEおよび拡散チャンバーFで溶融ポリフェニレンスルフィド樹脂と不活性ガスの完全相溶状態が形成され、続いてノズルGを通して金型IのキャビティHに射出され、圧力解放されて微細かつ均一な発泡状態を有するポリフェニレンスルフィド樹脂発泡成形品が形成される。
【0045】ここで、金型I内にカウンタープレッシャーを負荷させることにより発泡径をコントロールすることも可能であり、必要に応じてカウンタープレッシャー用ガスボンベLから不活性ガスを供給してもかまわない。その際の圧力としては特に制限は無いが、0．5〜15MPaの範囲であることが好ましい。
【0046】また、金型I内で急激に圧力低下させて発泡を促進させる方法として、溶融したポリフェニレンスルフィド樹脂を金型IのキャビティH内に射出した後、金型のコアの一部または全部を後退させて金型内容積を急激に増大させてもかまわない。
【0047】本発明のポリフェニレンスルフィド樹脂発泡成形品は、一般にポリフェニレンスルフィド樹脂が適用し得るあらゆる用途に適用可能である。例えば、軽量化要求の大きい自動車分野としては、シリンダーヘッドカバー、タイミングベルトカバー、バランスシャフトギア、オイル制動バルブ、オイルレベルゲージ、オイルクリーナーケース、ラジエータータンク、ウォーターポンプインペラー、サーモスタットハウジング、クーリングファン、インタークーラータンク、エアーダクト、エアコントロールバルブ、エアレギュレーター、エアフローメーターハウジング、エアーダクトインテーク、サイレンサー、レゾネーター、排ガスポンプサイドシール、排ガスバルブ、キャブレター、ガソリン噴射ノズル、ピストンバルブ、キャブレターバルブ、サージタンク、フューエルフィルターハウジング、フューエルストレーナー、フューエルセジメンタルケース、キャニスター、EGIチューブ、ソレノイドバルブ、ガソリンフロート、ガソリンチャンバー、フューエルチェックバルブ、フューエルインジェクター、フューエルインジェクターコネクター、フューエルインジェクターノズルカバー、フューエルフィラーキャップ、マスターシリンダーピストン、クラッチオイルリザーバー、スラストワッシャー、シフトアームコーティング、シフトレバーノブ、トランスミッションケース、トルコンスラストワッシャー、トランスミッションブッシュ、パワーステアリングタンク、ステアリングコラムカバー、ステアリングホーンパッド、ステアリングボールジョイント、ホイールフルキャップ、ホイールキャップセンター、ホイールセンターハブキャップ、ブレーキオイルリザーバー、ブレーキオイルフロート、ブレーキリザーバーキャップ、サイドブレーキワイヤープロテクター、ラジエーターグリル、フロントエンドバンパー、リアエンドバンパー、バンパーモール、フロントフェンダー、サイドミラーステイ、サイドミラーハウジング、エンブレム、リトラクタブルヘッドランプカバー、電動ミラーベース、フューエルリッド、ボンネットフードルーバー、エクストラクトグリル、ドア、サイドルーバー、ドアラッチカバー、ドアサイドモール、アウタードアハンドル、ピラールーバー、トランクロアーバックフィニシャー、トランクリアエプロン、ハッチバックスライドブラケット、ライセンスプレート、ライセンスプレートポケット、フューエルリッド、サンルーフフレーム、サイドモール、ウィンドウピボット、ウィンドウガラススライダー、ウィンドウモール、エアースポイラー、インストゥルメントパネルコア、リッドアウター、センタークラスター、スイッチ、アッパーガーニッシュ、リッドクラスター、メーターフード、メーターパネル、グローブボックス、チェンジレバーカバー、グローブボックスリッド、グローブボックスノブ、グローブドアアウター、アッシュトレイランプハウジング、アッシュトレイパネル、サンバイザーブラケット、サンバイザーシャフト、サンバイザーホルダー、ピラーガーニッシュ、ルームミラーステイ、レギュレーターハンドル、ドアトリム、インサイドドアロックノブ、インナーロックノブ、ウィンドウレギュレーターハンドル、ウィンドウレギュレーターハンドルノブ、ルーフサイドレールガーニッシュ、アームレストインサート、アームレストベース、アームレストガイド、リアシェルフサイド、ヘッドレストガイド、シートベルトタングプレート、シートベルトリトラクターギア、シートベルトバックル、シートベルトスルーアンカー、リッドクラスター、安全ベルト機構部品、クーラーシロッコファン、クーラーバキュームポンプ、エアコンマグネットクラッチボビン、エアコンアクチュエーター、コンプレッサーバルブ、エアーベンチレーションフィン、エアコン調節ツマミ、ヒーターコアタンク、ヒーターバルブ、ジェネレーターコイルボビン、ジェネレーターカバー、ジェネレーターブッシュ、サーキットボード、ブラシホルダー、コンデンサーケース、レギュレーターケース、スターターレバー、スターターコイルボビン、スターターインターバルギア、ディストリビューターポイントブッシュ、イグニッションコイルケース、イグニッションコイルボビン、ディストリビューター絶縁端子、ディストリビューターキャップ、スリーブベアリング、ヘリカルギアー、バキュームコントローラー、ジャンクションボックス、ワイヤーハーネスコネクター、リレーターミナルベースケースコイルボビン、ヒューズボックス、スイッチベース、リレーケース、各種スイッチ基板、ランプソケット、ランプリフレクター、バックホーンハウジング、サイレントギア、パワーウィンドウスイッチ基板ケース、ワイパーレバー、ウォッシャーモーターハウジン

グ、ワイパーモーターインシュレーター、ワイパーアームヘッドカバー、ウォッシャーノズル、ワイパーアームヘッド、スピードメータードリブンギア、スピードメーターコントロール、メーターコネクター、回転センサー、スピードセンサー、パワーシートギアハウジング、ブラシホルダー、コンミュテーター、モーターギア、ボンネットクリップ、モールクリップ、内装クリップ、バンパークリップ、電気配線用バンドクリップ、アンテナインナーチューブ、フェンダー、スポイラー、ルーフレール、テールゲート、およびバンパーなどが挙げられる。

【0048】電気・電子用途としては、センサー、LEDランプ、コネクター、ソケット、抵抗器、リレーケース、スイッチ、コイルボビン、コンデンサー、バリコンケース、光ピックアップ、発振子、各種端子板、変成器、プラグ、プリント基板、チューナー、スピーカー、マイクロフォン、ヘッドフォン、小型モーター、磁気ヘッドベース、パワーモジュール、半導体、液晶、FDDキャリッジ、FDDシャーシ、モーターブラッシュホルダー、パラボラアンテナ、コンピューター関連部品、VTR部品、テレビ部品、アイロン、ヘアードライヤー、炊飯器部品、電子レンジ部品、音響部品、オーディオ・レーザーディスク（登録商標）・コンパクトディスク等の音声機器部品、照明部品、冷蔵庫部品、エアコン部品、タイプライター部品、ワードプロセッサー部品、オフィスコンピューター関連部品、電話器関連部品、ファクシミリ関連部品、および複写機関連部品などが挙げられる。

【0049】その他の用途としては、洗浄用治具、モーター部品、ライター、タイプライター等の機械関連部品、顕微鏡、双眼鏡、カメラ、時計等の光学機器、精密機械関連部品、水道蛇口コマ、混合水栓、ポンプ部品、パイプジョイント、水量調節弁、逃がし弁、湯温センサー、水量センサー、水道メーターハウジングなどの水廻り部品、医療機器、建材関係部品、家具用部品などが挙げられる。

【0050】

【実施例】以下に実施例を示し、本発明を更に具体的に説明する。本発明はこれら実施例の記載に限定されるものではない。また、実施例および比較例中に示された配合割合において特に注釈のない「％」は、全て重量％を意味する。

【0051】また、各種特性の評価は次に記載の方法により行った。

［ポリフェニレンスルフィド樹脂のメルトインデックス（MI）］

・130℃の熱風乾燥機で3時間乾燥したポリフェニレンスルフィド樹脂について、長さ8mm、ノズル径2．095mmのオリフィスを用い、荷重5kg、温度315．6℃、サンプル量7g、サンプル仕込みから測定開始までのプレヒート時間5minでの条件で測定した。単位はg／10min。

［射出成形機］

・最大型締力　2000kN

・スクリュー径　42mm（L／D＝28）

［比重］

・得られた成形品を用い、ASTM　D792に準じて測定した。

［気泡径］

・顕微鏡を用いた形態観察により、任意の気泡500個について気泡径を測定し、その平均値を気泡サイズとした。

［機械特性］

・引張特性：　ASTM　D638に準じて測定した。

・曲げ特性：　ASTM　D790に準じて測定した。

［そり、ひけ］

・得られた発泡成形品のそり、ヒケを目視により評価した。

［参考例1］ポリフェニレンスルフィド樹脂（A－1）の製造

撹拌機付きオートクレーブに、水硫化ナトリウム水溶液4．67kg（水硫化ナトリウム25モル）、50％水酸化ナトリウム2kg（水酸化ナトリウム25モル）ならびにN－メチル－2－ピロリドン8kgを仕込み、撹拌しながら徐々に昇温し、水3．8kgを含む留出水4．1Lを除去した。残留混合物に1，4－ジクロロベンゼン3．75kg（25．5モル）ならびにN－メチル－2－ピロリドン2kgを加えて230℃で1時間加熱した。反応生成物を温水で5回洗浄後、90℃、pH4の酢酸水溶液25L中に投入し、1時間撹拌した。ポリフェニレンスルフィド樹脂を沪過し、沪液のpHが7になるまで90℃のイオン交換水で洗浄した後、80℃で24時間真空乾燥した。得られたポリフェニレンスルフィド樹脂のメルトインデックスの自然対数値は8．52であった。

［参考例2］ポリフェニレンスルフィド樹脂（A－2）の製造

参考例1で得られたポリフェニレンスルフィド樹脂を、スパイラル型撹拌翼を備えた撹拌釜に仕込み、1L／minの空気を送り込みながら回転数60rpmで7時間撹拌した。得られたポリフェニレンスルフィド樹脂のメルトインデックスの自然対数値は5．70であった。

［参考例3］ポリフェニレンスルフィド樹脂（A－3）の製造

参考例1で得られたポリフェニレンスルフィド樹脂を、スパイラル型撹拌翼を備えた撹拌釜に仕込み、1L／minの空気を送り込みながら回転数60rpmで9時間撹拌した。得られたポリフェニレンスルフィド樹脂のメルトインデックスの自然対数値は4．00であった。

［参考例4］ポリフェニレンスルフィド樹脂（A－4）

の製造
撹拌機付きオートクレーブに、水硫化ナトリウム水溶液４．６７ｋｇ（水硫化ナトリウム２５モル）、５０％水酸化ナトリウム２ｋｇ（水酸化ナトリウム２５モル）ならびにＮ－メチル－２－ピロリドン８ｋｇを仕込み、撹拌しながら徐々に昇温し、水３．８ｋｇを含む留出水４．１Ｌを除去した。残留混合物に１，４－ジクロロベンゼン３．７５ｋｇ（２５．５モル）ならびにＮ－メチル－２－ピロリドン２ｋｇを加えて２３０℃で２５分加熱した。反応生成物を温水で５回洗浄後、９０℃、ｐＨ４の酢酸水溶液２５Ｌ中に投入し、４５分撹拌した。ポリフェニレンスルフィド樹脂を沪過し、沪液のｐＨが７になるまで９０℃のイオン交換水で洗浄した後、８０℃で２４時間真空乾燥した。得られたポリフェニレンスルフィド樹脂のメルトインデックスの自然対数値は８．９８であった。

［参考例５］ポリフェニレンスルフィド樹脂（Ａ－５）の製造

参考例１で得られたポリフェニレンスルフィド樹脂をスパイラル型撹拌翼を備えた撹拌釜に仕込み、１Ｌ／ｍｉｎの空気を送り込みながら回転数６０ｒｐｍで１４時間撹拌した。得られたポリフェニレンスルフィド樹脂のメルトインデックスの自然対数値は２．３０であった。なお、以下の実施例では全て図１に構成概略を示した態様の射出成形機を使用した。シリンダー温度はノズル側からホッパー側に向けて、３００℃／２９０℃／２８０℃／２７０℃のように設定した。また、成形品はＡＳＴＭ１号引張試験片および５０ｍｍ×５０ｍｍ×３０ｍｍサイズで厚み１．５ｍｍの箱の２種を成形し、前者で比重、引張特性、曲げ特性を測定し、後者でソリ、ヒケの評価を行った。金型温度はいずれの場合も３０℃とした。超臨界流体としては窒素または炭酸ガスを使用し、注入量はポリフェニレンスルフィド樹脂またはポリフェニレンスルフィド樹脂組成物１００ｇに対して１ｇとした。

［実施例１～３］参考例１～３で製造したポリフェニレンスルフィド樹脂Ａ－１，Ａ－２およびＡ－３のそれぞれに対して、ガラス繊維（旭ファイバーガラス製ＪＡ５２３）を４０重量％溶融混練した材料を使用し、超臨界流体として窒素ガスを用いて超臨界発泡射出成形を行った。得られた成形品の物性および外観の評価結果を表１に示す。

［実施例４～６］超臨界流体として炭酸ガスを用いた以外は、実施例１～３と同様にして超臨界発泡射出成形を行った。得られた成形品の物性および外観の評価結果を表１に併せて示す。

［実施例７～９］参考例１～３で製造したポリフェニレンスルフィド樹脂Ａ－１，Ａ－２およびＡ－３のそれぞれに対して、ガラス繊維（旭ファイバーガラス製ＪＡ５２３）４５重量％および炭酸カルシウム（同和カルファイン製ＫＳＳ１０００）２０重量％を溶融混練した材料を使用し、超臨界流体として窒素ガスを用いて超臨界発泡射出成形を行った。得られた成形品の物性および外観の評価結果を表１に併せて示す。

［実施例１０～１２］超臨界流体として炭酸ガスを用いた以外は、実施例７～９と同様にして超臨界発泡射出成形を行った。得られた成形品の物性及び外観の評価結果を表１に併せて示す。

［実施例１３～１５］参考例１～３で製造したポリフェニレンスルフィド樹脂Ａ－１，Ａ－２およびＡ－３のそれぞれに対して、ＰＡＮ系炭素繊維（東レ製Ｔ３００）を３０重量％溶融混練した材料を使用し、超臨界流体として窒素ガスを用いて超臨界発泡射出成形を行った。得られた成形品の物性および外観の評価結果を表１に併せて示す。

［実施例１６～１８］超臨界流体として炭酸ガスを用いた以外は、実施例１３～１５と同様にして超臨界発泡射出成形を行った。得られた成形品の物性および外観の評価結果を表１に併せて示す。

【００５２】

【表１】

表1

実施例	ポリフェニレンスルフィド樹脂	フィラー 種類／配合量	超臨界流体	比重	気泡径 (μm)	引張特性 強度 (MPa)	引張特性 破断伸度 (%)	曲げ特性 強度 (MPa)	曲げ特性 弾性率 (GPa)	そり*	ひけ*
1	A－1（参考例1）	GF／40wt%	窒素	1.53	5.2	165	2.5	209	10.0	○	○
2	A－2（参考例2）	GF／40wt%	窒素	1.54	4.7	168	2.9	215	10.2	○	○
3	A－3（参考例3）	GF／40wt%	窒素	1.51	5.1	165	2.6	208	9.9	○	○
4	A－1（参考例1）	GF／40wt%	炭酸ガス	1.51	4.8	168	2.8	213	10.2	○	○
5	A－2（参考例2）	GF／40wt%	炭酸ガス	1.51	4.5	171	3.1	217	10.4	○	○
6	A－3（参考例3）	GF／40wt%	炭酸ガス	1.51	4.7	167	2.9	213	10.1	○	○
7	A－1（参考例1）	GF／45wt% 炭繊／20wt%	窒素	1.80	4.8	118	1.3	157	14.0	○	○
8	A－2（参考例2）	GF／45wt% 炭繊／20wt%	窒素	1.81	4.5	121	1.7	161	14.2	○	○
9	A－3（参考例3）	GF／45wt% 炭繊／20wt%	窒素	1.81	4.7	117	1.4	156	13.9	○	○
10	A－1（参考例1）	GF／45wt% 炭繊／20wt%	炭酸ガス	1.78	4.6	121	1.5	160	14.2	○	○
11	A－2（参考例2）	GF／45wt% 炭繊／20wt%	炭酸ガス	1.78	4.3	124	1.9	163	14.4	○	○
12	A－3（参考例3）	GF／45wt% 炭繊／20wt%	炭酸ガス	1.78	4.6	120	1.6	159	14.1	○	○
13	A－1（参考例1）	CF／30wt%	窒素	1.32	5.3	159	1.7	202	16.0	○	○
14	A－2（参考例2）	CF／30wt%	窒素	1.33	4.7	163	2.1	208	16.1	○	○
15	A－3（参考例3）	CF／30wt%	窒素	1.33	5.2	158	1.8	201	15.9	○	○
16	A－1（参考例1）	CF／30wt%	炭酸ガス	1.30	4.9	163	2.0	206	16.1	○	○
17	A－2（参考例2）	CF／30wt%	炭酸ガス	1.29	4.5	166	2.4	210	16.4	○	○
18	A－3（参考例3）	CF／30wt%	炭酸ガス	1.29	4.8	162	2.1	205	16.0	○	○

* ○：ソリ、ヒケが殆ど認められない　△：ソリ、ヒケが若干認められる　×：著しいソリ、ヒケが認められる

【0053】［参考例6～8］超臨界流体を注入しないこと以外は、実施例1～3と同様にして射出成形を行った。すなわち、通常の射出成形である。得られた成形品の物性および外観の評価結果を表2に示す。

［参考例9～11］超臨界流体を注入しないこと以外は、実施例7～9と同様にして射出成形を行った。すなわち、通常の射出成形である。得られた成形品の物性および外観の評価結果を表2に併せて示す。

［参考例12～14］超臨界流体を注入しないこと以外は、実施例13～15と同様にして射出成形を行った。すなわち、通常の射出成形である。得られた成形品の物性および外観の評価結果を表2に併せて示す。

【0054】

【表2】

表2

参考例	ポリフェニレンスルフィド樹脂	フィラー 種類／配合量	超臨界流体	比重	気泡径 (μm)	引張特性 強度 (MPa)	引張特性 破断伸度 (%)	曲げ特性 強度 (MPa)	曲げ特性 弾性率 (GPa)	そり*	ひけ*
6	A－1（参考例1）	GF／40wt%	－	1.67	－	190	3.1	260	12.6	×	△
7	A－2（参考例2）	GF／40wt%	－	1.67	－	195	3.5	268	12.6	×	△
8	A－3（参考例3）	GF／40wt%	－	1.67	－	192	3.8	263	12.4	×	△
9	A－1（参考例1）	GF／45wt% 炭繊／20wt%	－	1.96	－	132	2.0	193	17.5	×	△
10	A－2（参考例2）	GF／45wt% 炭繊／20wt%	－	1.96	－	139	2.1	200	17.5	×	△
11	A－3（参考例3）	GF／45wt% 炭繊／20wt%	－	1.96	－	136	2.4	198	17.3	×	△
12	A－1（参考例1）	CF／30wt%	－	1.44	－	183	2.4	252	20.0	×	△
13	A－2（参考例2）	CF／30wt%	－	1.44	－	189	2.8	259	20.0	×	△
14	A－3（参考例3）	CF／30wt%	－	1.44	－	185	3.0	256	19.8	×	△

* ○：ソリ、ヒケが殆ど認められない　△：ソリ、ヒケが若干認められる　×：著しいソリ、ヒケが認められる

【0055】［比較例1～2］参考例4～5で製造したポリフェニレンスルフィド樹脂A－4またはA－5を使用したこと以外は、実施例1と同様にして超臨界発泡射出成形を行った。得られた成形品の物性および外観の評価結果を表3に示す。

［比較例3～4］参考例4～5で製造したポリフェニレンスルフィド樹脂A－4またはA－5を使用したこと以外は、実施例4と同様にして超臨界発泡射出成形を行った。得られた成形品の物性および外観の評価結果を表3に併せて示す。

［比較例5～6］参考例4～5で製造したポリフェニレンスルフィド樹脂A－4またはA－5を使用したこと以外は、実施例7と同様にして超臨界発泡射出成形を行った。得られた成形品の物性および外観の評価結果を表3に併せて示す。

［比較例7～8］参考例4～5で製造したポリフェニレンスルフィド樹脂A－4またはA－5を使用したこと以外は、実施例10と同様にして超臨界発泡射出成形を行

った。得られた成形品の物性および外観の評価結果を表3に併せて示す。

［比較例9～10］参考例4～5で製造したポリフェニレンスルフィド樹脂A－4またはA－5を使用したこと以外は、実施例13と同様にして超臨界発泡射出成形を行った。得られた成形品の物性および外観の評価結果を表3に併せて示す。

［比較例11～12］参考例4～5で製造したポリフェニレンスルフィド樹脂A－4またはA－5を使用したこと以外は、実施例16と同様にして超臨界発泡射出成形を行った。得られた成形品の物性および外観の評価結果を表3に併せて示す。

［比較例13］参考例1で製造したポリフェニレンスルフィド樹脂A－1の60重量部に、ガラス繊維（旭ファイバーガラス製JA523）40重量部を溶融混練して得たペレット100重量部に、熱分解性発泡剤として5－フェニルテトラゾール（永和化成工業"セルテトラ" PT5）を0．5重量部をドライブレンドした材料を使用し、超臨界流体を使用しない以外は、実施例1と同様にして射出成形を行った。得られた成形品の物性および外観の評価結果を表3に示す。

［比較例14］参考例1で製造したポリフェニレンスルフィド樹脂A－1の35重量部にガラス繊維（旭ファイバーガラス製JA523）45重量部、炭酸カルシウム（同和カルファイン製KSS1000）20重量部を溶融混練して得たペレット100重量部に、熱分解性発泡剤として5－フェニルテトラゾール（永和化成工業"セルテトラ" PT5）を0．5重量部をドライブレンドした材料を使用し、超臨界流体を使用しない以外は、実施例7と同様にして射出成形を行った。得られた成形品の物性および外観の評価結果を表3に併せて示す。

［比較例15］参考例1で製造したポリフェニレンスルフィド樹脂A－1の70重量部にPAN系炭素繊維（東レ製T300）を30重量%溶融混練して得たペレット100重量部に、熱分解性発泡剤として5－フェニルテトラゾール（永和化成工業"セルテトラ" PT5）を0．5重量部をドライブレンドした材料を使用し、超臨界流体を使用しない以外は、実施例13と同様にして射出成形を行った。得られた成形品の物性および外観の評価結果を表3に併せて示す。

【0056】

【表3】

表 3

比較例	ポリフェニレンスルフィド樹脂	フィラー 種類／配合量	超臨界流体	比重	気泡径 (μm)	引張特性 強度 (MPa)	引張特性 破断伸度 (%)	曲げ特性 強度 (MPa)	曲げ特性 弾性率 (GPa)	そり*	ひけ*
1	A－4（参考例4）	GF／40wt%	窒素	1.60	7.1	130	2.0	185	9.5	○	○
2	A－5（参考例5）	GF／40wt%	窒素	1.60	7.2	133	2.2	188	9.4	○	○
3	A－4（参考例4）	GF／40wt%	炭酸ガス	1.59	6.9	134	2.1	188	9.6	○	○
4	A－5（参考例5）	GF／40wt%	炭酸ガス	1.60	6.8	136	2.5	191	9.6	○	○
5	A－4（参考例4）	GF／45wt% 炭カル／20wt%	窒素	1.88	6.4	94	1.1	137	13.1	○	○
6	A－5（参考例5）	GF／45wt% 炭カル／20wt%	窒素	1.89	6.3	97	1.4	141	13.0	○	○
7	A－4（参考例4）	GF／45wt% 炭カル／20wt%	炭酸ガス	1.88	6.2	95	1.2	140	13.3	○	○
8	A－5（参考例5）	GF／45wt% 炭カル／20wt%	炭酸ガス	1.88	6.2	99	1.5	143	13.4	○	○
9	A－4（参考例4）	CF／30wt%	窒素	1.37	7.2	126	1.7	175	15.0	○	○
10	A－5（参考例5）	CF／30wt%	窒素	1.38	7.1	130	2.1	178	14.9	○	○
11	A－4（参考例4）	CF／30wt%	炭酸ガス	1.38	6.8	130	2.0	178	15.2	○	○
12	A－5（参考例5）	CF／30wt%	炭酸ガス	1.38	6.9	133	2.3	181	15.2	○	○
13	A－1（参考例1）	GF／40wt%	化学発泡	1.53	31.4	57	1.3	160	10.0	○	○
14	A－1（参考例1）	GF／45wt% 炭カル／20wt%	化学発泡	1.80	28.9	41	1.0	119	14.1	○	○
15	A－1（参考例1）	CF／30wt%	化学発泡	1.32	33.5	56	1.2	149	16.1	○	○

＊ ○：ソリ、ヒケが殆ど認められない　△：ソリ、ヒケが若干認められる　×：著しいソリ、ヒケが認められる

【0057】実施例1～3の結果より、メルトインデックスの自然対数値が3．8～8．8の範囲にあるポリフェニレンスルフィド樹脂にガラス繊維を配合した組成物を、超臨界発泡射出成形することにより、顕微鏡観察による発泡形態が微細・均一であり、軽量かつ物性に優れた成形品が得られることがわかる。また、ソリやヒケのない箱状成形品が得られることがわかる。実施例4～6の結果より、超臨界流体を窒素から炭酸ガスに変更しても、窒素を用いた実施例1～3と同様の効果が得られることがわかる。実施例7～9の結果より、メルトインデックスの自然対数値が3．8～8．8の範囲にあるポリフェニレンスルフィド樹脂に、ガラス繊維および炭酸カルシウムを配合した組成物を超臨界発泡射出成形することにより、発泡が微細・均一であり、軽量かつ物性に優れた成形品が得られることがわかる。また、ソリやヒケのない箱状成形品が得られることがわかる。実施例10～12の結果より、超臨界流体を窒素から炭酸ガスに変更しても、窒素を用いた実施例7～9と同様の効果が得られることがわかる。実施例13～15の結果より、メルトインデックスの自然対数値が3．8～8．8の範囲

にあるポリフェニレンスルフィド樹脂に炭素繊維を配合した組成物を超臨界発泡射出成形することにより、発泡が微細・均一であり、軽量かつ物性に優れた成形品が得られることがわかる。また、ソリやヒケのない箱状成形品が得られることがわかる。実施例１６～１８の結果より、超臨界流体を窒素から炭酸ガスに変更しても、窒素を用いた実施例１３～１５と同様の効果が得られることがわかる。参考例６～１４の結果より、通常の射出成形で得られた成形品は、機械物性は優れているが、箱状成形品ではソリやヒケが観察され、この点で問題のあることがわかる。比較例１～４の結果より、メルトインデックスの自然対数が３．８～８．８の範囲にないポリフェニレンスルフィド樹脂にガラス繊維を配合した組成物を、超臨界発泡射出成形した場合には、ソリ、ヒケのない成形品が得られるものの、比重、気泡径が大きく、物性が低いことがわかる。比較例５～８の結果より、メルトインデックスの自然対数が３．８～８．８の範囲にないポリフェニレンスルフィド樹脂にガラス繊維および炭酸カルシウムを配合した組成物を、超臨界発泡射出成形した場合には、ソリ、ヒケのない成形品が得られるものの、比重、気泡径が大きく、物性が低いことがわかる。比較例９～１２の結果より、メルトインデックスの自然対数が３．８～８．８の範囲にないポリフェニレンスルフィド樹脂に炭素繊維を配合した組成物を、超臨界発泡射出成形した場合には、ソリ、ヒケのない成形品が得られるものの、比重、気泡径が大きく、物性が低いことがわかる。比較例１３の結果より、メルトインデックスの自然対数が３．８～８．８の範囲にあるポリフェニレンスルフィド樹脂にガラス繊維を配合した組成物を用いても、化学発泡剤による発泡射出成形した場合には、ソリ、ヒケのない成形品が得られるものの、比重、気泡径が大きく、物性が低いことがわかる。比較例１４の結果より、メルトインデックスの自然対数が３．８～８．８の範囲にあるポリフェニレンスルフィド樹脂にガラス繊維および炭酸カルシウムを配合した組成物を用いても、化学発泡剤による発泡射出成形した場合には、ソリ、ヒケのない成形品が得られるものの、比重、気泡径が大きく、物性が低いことがわかる。比較例１５の結果より、メルトインデックスの自然対数が３．８～８．８の範囲にあるポリフェニレンスルフィド樹脂に炭素繊維を配合した組成物を用いても、化学発泡剤による発泡射出成形した場合には、ソリ、ヒケのない成形品が得られるものの、比重、気泡径が大きく、物性が低いことがわかる。

【００５８】

【発明の効果】以上説明したように、本発明のポリフェニレンスルフィド樹脂発泡成形品は、ポリフェニレンスルフィド樹脂の特性を保持したまま、微細かつ均一な発泡状態を有するものであり、軽量化が可能である上に、ヒケやソリが少ないという優れた特性を有するものである。したがって、本発明によれば、各種ポリフェニレンスルフィド樹脂成形品の軽量化と共に、外観および寸法精度の向上を図ることができる。

【図面の簡単な説明】

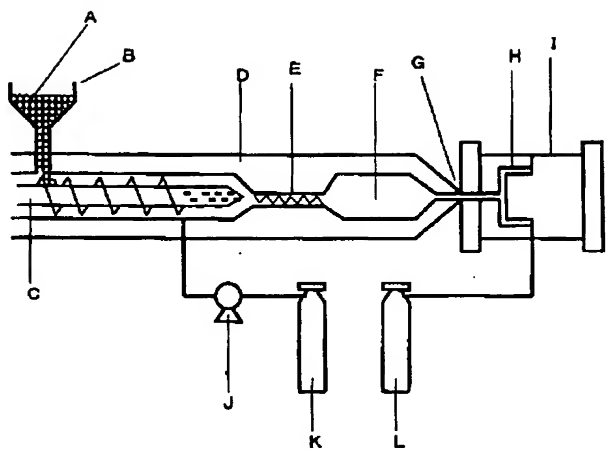
【図１】本発明で使用される射出成形機の一例を示す概略構成図である。

【符号の説明】

A　ポリフェニレンスルフィド樹脂ペレット
B　ホッパー
C　スクリュー
D　シリンダー
E　スタティックミキサー
F　拡散チャンバー
G　ノズル
H　キャビティ（成形品）
I　金型
J　昇圧ポンプ
K　ガスボンベ
L　カウンタープレッシャー用ガスボンベ

【図1】

【図1】



フロントページの続き

(51)Int.Cl.⁷	識別記号	FI	テーマコード(参考)
C08L 81:02		C08L 81:02	

DERWENT-ACC-NO: 1987-104351

DERWENT-WEEK: 198715

TITLE: Foamed polycarbonate resin for optical use - consists of polycarbonate of low chlorine content, and organic phosphonate

PATENT-ASSIGNEE: TEIJIN CHEM LTD[TEIQ]

PRIORITY-DATA: 1985JP-0189899 (August 30, 1985)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
JP 62050801 A	March 5, 1987	N/A	006	N/A
JP 91041802 B	June 25, 1991	N/A	000	N/A

APPLICATION-DATA:

PUB-NO	APPL-DESCRIPTOR	APPL-NO	APPL-DATE
JP 62050801A	N/A	1985JP-0189899	August 30, 1985
JP 91041802B	N/A	1985JP-0189899	August 30, 1985

INT-CL (IPC): B41M005/26, C08L069/00 , G02B001/04 , G11B007/24

ABSTRACTED-PUB-NO: JP 62050801A

BASIC-ABSTRACT:

Compsn. consists of polycarbonate of average molecular wt. 13,000-18,000 with chlorine content less than 0.0040 wt.%; and 0.0001-0.01 wt.% organic phosphonite based on the weight of the polycarbonate. Compsn. is melt formed.

USE/ADVANTAGE - As parts of information-processing devices or plastic lenses.
Common thermoplastic techniques are employed (injection moulding, compression

moulding etc.). Good transparency and optical distortion characteristic etc.
are provided.

In an example, polycarbonate (av. molecular wt. 14,8000, chlorine content
0.0015 wt.% was pelletised with 0.002 wt.% tetrakis(2,4-ditert.-butylphen-
yl)4,4'-biphenylene diphosphonite. Discs 1.2 mm thick and 120 mm in dia. were
injection-moulded from the pellets. Light transmissiti transmissivity and
birefringence determined were 91% and 9 nm, respectively.

CHOSEN-DRAWING: Dwg.0/0

TITLE-TERMS: **FOAM POLYCARBONATE** RESIN **OPTICAL** CONSIST **POLYCARBONATE** LOW
CHLORINE CONTENT ORGANIC PHOSPHONATE

DERWENT-CLASS: A23 A89 P75 P81 T03 W04

CPI-CODES: A05-E06B; A08-M09C; A09-A02; A12-L02A; A12-L03;

EPI-CODES: T03-B01A; W04-C01;

UNLINKED-DERWENT-REGISTRY-NUMBERS: 5343U

POLYMER-MULTIPUNCH-CODES-AND-KEY-SERIALS:
Key Serials: 0204 0231 1292 2319 2462 2465 2510 2544 2585 2588 2594 2595 2654
2676 3310 2851 2545
Multipunch Codes: 014 04- 143 155 157 158 228 342 437 456 458 461 463 476 516
517 522 523 528 57& 575 583 589 596 649 725

SECONDARY-ACC-NO:
CPI Secondary Accession Numbers: C1987-043369
Non-CPI Secondary Accession Numbers: N1987-078242

⑲日本国特許庁（JP）　　⑪特許出願公開

⑫公開特許公報（A）　　昭62-50801

⑤Int.Cl.⁴	識別記号	庁内整理番号	㊸公開　昭和62年(1987) 3月5日
G 02 B 1/04		7915-2H	
B 41 M 5/26		7447-2H	
G 11 B 7/24		8421-5D	審査請求　未請求　発明の数 1　（全6頁）

㊹発明の名称　光学用成形品

㉑特　　願　昭60-189899

㉒出　　願　昭60(1985) 8月30日

⑫発 明 者　宮 内　正 嘉　松山市水泥町22-63

⑪出 願 人　帝人化成株式会社　東京都港区西新橋1丁目6番21号

⑭代 理 人　弁理士 前田 純博

明　　細　　書

1.　発明の名称

光学用成形品

2.　特許請求の範囲

ポリカーボネートの重量を基準にして0.0001～0.01重量%の有機ホスホナイトが配合されておりかつ塩素含有量が0.0040重量%未満である平均分子量13,000～18,000のポリカーボネートを主成分とする樹脂組成物を溶融成形してなる光学用成形品。

3.　発明の詳細な説明

＜産業上の利用分野＞

本発明は光学用成形品に関し、更に詳しくは少量の安定剤を含有する光度に精製されたポリカーボネートから成形された優れた性能を有する光学用成形品に関する。

＜従来技術＞

最近ポリカーボネートが光学用途、特に情報処理機器部品の材料として、脚光を浴びるようになつた。かかる用途の中でも特に情報記録用基盤として使用されるときは、その表面に例えば金属や金属化合物の薄膜を付けたり、色素を含む層を付けたりする。又メガネ用レンズに使用されるときには表面硬度の改善，防曇，防眩などを目的とした薄膜を付けることが多い。かかる場合には基盤表面の化学的性質が重要な因子となる。

従来、一般のポリカーボネートは僅かではあるが、溶媒として使用された塩化メチレンや未反応残基であるクロロホーメート基を有する化合物などの塩素化合物を含有しており、これらの化合物は300℃以上の如き高温で成形するときに分解して酸性物質を生じ、金型腐食の原因となつたり、更に成形品の表面に金属，金属化合物などの薄膜，色素を含有する薄膜，或はその他の薄膜が付けられるときには、それらの薄膜，色素などを変質させる原因となる。しかして、かかる塩素化合物を可及的に除去したポリカーボネートは，高

温成形において、酸性物質を生じることはないが、例えば350℃以上の成形においては、焼けや着色を回避することはできなかつた。かかる場合に、従来の一般用ポリカーボネートの熱安定剤として最も広く使用されている亜リン酸エステルを配合すると、焼けや着色は解消しうるが、得られた成形品を高温多湿の雰囲気下に長時間曝露するとポリカーボネートの平均分子量の低下をもたらすと同時にその表面に前記の薄膜を付けてあるときは、それらに対して悪影響を与えることがある。

＜発明の目的＞

本発明の目的は塩素系酸性物質を実質上問題のない程度にしか含まず、かつ高温，多湿の雰囲気下においてもその表面に付けられる金属や金属化合物の薄膜，その他の薄膜に悪影響を与えることのない光学用成形品を提供することにある。

＜発明の構成＞

本発明は、ポリカーボネートの重量を基準にして0.0001～0.01重量%の有機ホスホナイトが配合されておりかつ塩素含有量が0.0040重量%未満である、平均分子量13,000～18,000のポリカーボネートを主成分とする樹脂組成物を溶融成形してなる光学用成形品である。

本発明で使用されるポリカーボネートは2価フェノールとカーボネート先駆体との反応によつて得られる透明なものであり2価フェノールとしてはハイドロキノン，4,4'－ジオキシジフェニル，ビス（ヒドロキシフェニル）アルカン，ビス（ヒドロキシフェニル）シクロアルカン，ビス（ヒドロキシフェニル）エーテル，ビス（ヒドロキシフェニル）ケトン，ビス（ヒドロキシフェニル）スルフイド，ビス（ヒドロキシフェニル）スルホン，及びこれらの低級アルキル，ハロゲン等の置換体を挙げることができるが、2,2'－ビス（4－ヒドロキシフェニル）プロパン（以下ビスフェノールAという），1,1－ビス（4－ヒドロキシフェニル）エタン，2,2－ビス（4－ヒドロキシフェニル）－ヘキサフルオロプロパン等が好ましく使用できる。これらの2価フェノールは単体で、或は混合して使用することができる。更に本発明で使用されるポリカーボネートは、炭酸残基の一部が芳香族二塩基酸残基で置換されていてもよいし、分岐構造になつていてもよい。

これらのポリカーボネートは、20℃で塩化メチレン100mlに樹脂0.7g（＝C）を溶解した溶液の比粘度η_{sp}をオストワルド粘度計で測定し

$$\eta_{sp} / C = [\eta] + 0.45[\eta]^2 C$$

で得られる極限粘度の値を次の式(1)に代入して求められる平均分子量が13,000～18,000の範囲にあることが必要である。

$$[\eta] = 1.23 \times 10^{-4} \bar{M}^{0.83} \quad \cdots\cdots (1)$$

平均分子量が13,000未満では、得られた成形品の強度が実用に耐えないので適当でない。又18,000を超えるときは、成形品の光学的性質等に光学歪，色相，透明性などに問題を生じ易いので適当でない。

又、ポリカーボネートはその重合反応において使用された塩化メチレンや二価フェノールのクロロホーメート，或は末端にクロロホーメート基を有するオリゴマーやポリマーを含有しており、これらの含有量は通常一括して塩素の含有量で表わされる。300℃以上での溶融成形に使用するポリカーボネート或はその組成物の塩素含有量が0.0040重量%以上のときは、成形機内でこれらの塩素化合物が分解し、酸性物質を生じて、金型腐食の原因になつたり、更に成形品の表面に金属，金属化合物などの薄膜，色素を含有する薄膜，或はその他の薄膜が付けられるときには、それらの薄膜，色素などを変質させる原因になるので適当でない。塩素含有量が0.0040重量%未満のときは、これらの有害作用は製品の実用上からは無視しうる程度である。

また、ポリカーボネートは、その製造過程

において添加されたリン系安定剤，例えば亜リン酸エステル，有機ホスフインなどを含有していてもよいが、その含有量は、リン原子として0.0003重量%以下であることが望ましい。

本発明で使用されるポリカーボネートを主成分とする樹脂組成物は有機ホスホナイトをポリカーボネートの重量を基準にして0.0001～0.01重量%配合されたものである。更に好ましい配合量は0.0005～0.005重量%である。

ポリカーボネートの熱安定剤として有機ホスホナイトが有効であることは特開昭46－47877号及び特開昭55－81895号で知られており、その配合量は0.005～1.0重量%が適当であるとされている。

本発明者の検討によれば、本発明において使用する塩素含有量が0.0040重量%未満のポリカーボネート組成物においては、有機ホスホナイトの配合量を前記提案で好ましいとされている0.01～0.2重量%にしたときには成形時における熱安定効果は充分にみられたが、その成形品の表面の一部にアルミ蒸着を施し、高温・多湿の雰囲気に長時間曝露したときに、アルミ膜に穴があき光沢を失なつて変質する場合のあることが認められ、本発明の目的には適当でないことが判つた。塩素含有量の低い場合は有機ホスホナイトの量が0.005重量%以下でも有効であることが認められたが、0.0001重量%未満にしたときには成形時における熱安定効果が殆んどみられなかつた。

従つて本発明で使用されるポリカーボネート組成物は、ポリカーボネートの重量を基準にして、塩素含有量が0.0040重量%未満、好ましくは0.0020重量%以下であり、かつ、有機ホスホナイトが0.0001～0.01重量%，好ましくは0.0005～0.005重量%配合されたものである。

本発明に用いられる有機ホスホナイトは例えば、ジメチルメチルホスホナイト，ジエチルメチルホスホナイト，ジプロピルメチルホスホナイト，ジイソプロピルメチルホスホナイト，ジメチルエチルホスホナイト，ジエチルエチルホスホナイト，ジプロピルエチルホスホナイト，ジイソプロピルエチルホスホナイト，ジメチルプロピルホスホナイト，ジエチルプロピルホスホナイト，ジメチルイソプロピルホスホナイト，ジエチルイソプロピルホスホナイト，ジメチルブチルホスホナイト，ジエチルブチルホスホナイト，ジプロピルブチルホスホナイト，ジイソプロピルブチルホスホナイト，ジシクロヘキシルメチルホスホナイト，ジフエニルメチルホスホナイト，ジベンジルメチルホスホナイト，ジメチルフエニルホスホナイト，ジメチルベンジルホスホナイト，ジフエニルフエニルホスホナイト，フエニル－(2,4,6－トリメチルフエニル)ベンゼンホスホナイト，ビス(2,4,6－トリメチルフエニル)ベンゼンホスホナイト，ジフエニルベンゼンホスホナイト，ジノニルフエニルベンゼンホスホナイト，ジイソオクチルベンゼンホスホナイト，〔(3－エチルオキセタニル－3)－メチル〕－(2,4,6－トリメチルフエニル)ベンゼンホスホナイト，ジイソデシルベンゼンホスホナイト，テトラキス(2,4－ジターシヤリブチルフエニル)4,4′－ビフエニレンジホスホナイトなどを例示することができる。

更に本発明で使用される組成物には、ステアリルステアレート，モンタン酸ワツクス，グリセリンモノステアレート，ペンタエリスリトールのステアレートなどの高級脂肪酸と一価又は多価アルコールとのエステル又は部分エステル系の離型剤（0.01～0.5重量%），ベンゾトリアゾール系，アセトフエノン系，サリチル酸エステル系などの紫外線吸収剤（0.1～0.7重量%），エポキシ化大豆油，エポキシ化ポリブタジエン，ビスフエノールAのジグリシジルエーテル，フタル酸ジグリ

シジルエステルなどのエポキシ化合物(0.01～1.0重量%)などを配合することができる。

本発明で使用されるポリカーボネート樹脂組成物はポリカーボネートと有機ホスホナイトを混合することによつて得られる。例えばタンブラー,V型ブレンダー,スーパーミキサー等によつてポリカーボネートの粉末又はペレットと有機ホスホナイトを簡単に混合することができる。またポリカーボネートの溶液に有機ホスホナイトを混合し、次いで溶媒を除去するなどの公知の手段によつて容易に調製することができる。

更にポリカーボネートの粉末又はペレットと有機ホスホナイトを連続的に押出し機に投入することによつても調製できる。例えば溶融押出しの如き配合方法を採用したときは有機ホスホナイトは他のリン化合物に変化することが予想されるが、そのような場合も本発明の範囲内に含まれるものとする。

本発明の光学用成形品はインジエクション成形,コンプレッション成形,或はインジエクシヨン－コンプレッション成形などによつて成形されるが、特に好ましいインジエクシヨン成形の成形条件は樹脂温度320～380℃,金型温度70～120℃である。

本発明の光学用成形品は、光線透過率が90%前後で極めて透明であり、かつ、複屈折で代表される光学歪が非常に小さいので、成形品中での屈折現象が殆んどなく、また、前記の如き種々の薄膜を付けても、それらに変質を生ずることがないなどの優れた性能を有するので、レンズ,プリズム,フレネルレンズ或は各種情報記録ディスク等の基盤として充分に実用に供しうるものである。

＜発明の効果＞

本発明の成形品は、高度に精製されたポリカーボネートに微少量の安定剤を配合した組成物を成形したものであるため、透明性,光学歪などが極めて優れており、更に、金属や金属化合物或は色素などの記録材料を含む薄膜,或は表面硬度,防曇,防眩などのための薄膜を付けてもその耐久性に優れるなどの光学用成形品としての必要な特性を充分に具備するものである。

＜実施例＞

以下、実施例及び比較例を挙げて本発明を説明する。なお、成形盤の複屈折,透過率の測定と蒸着品の評価(外観判定)は以下の方法によつた。

複屈折の測定

ペレットを3オンス射出成形機(ネオマット150／75型－住友重機工業社製)を用い、樹脂温度350℃,金型温度110℃で厚さ1.2mm,直径120mmの円盤に成形し、溝尻光学工業所製偏光解析装置を用いて中心から30mm周辺部に向かつて測定しnmで表示した。

透過率の測定

上記、成形円盤を日立自記分光光度計U－3400形で500～1000nmの波長範囲で測定し、透過率を%で表示した。

蒸着品の評価

真空蒸着装置のベルジャー内に前述した成形板を入れ10^{-5}トールでアルミニウムを片面のみ蒸着し、ウレタン樹脂を塗布したのち、湿度95%RH,温度85℃の雰囲気の恒温恒湿機に72時間放置し、処理前後に発生したピンホールの数を数えて評価した。ピンホールが発生すると情報を正確に記録することができないので好ましくない。

(実施例1～3)

平均分子量14,900のポリカーボネート樹脂粉末に第1表記載の割合で有機ホスホナイトを配合し、30mmφベント付き押出機を用いて260℃でスレッドを押し出しカッターで切断してペレットを得た。ペレットの平均分子量および塩素含有量は第1表のとおりであつた。

得られたペレットを3オンスの射出成形機を

用い樹脂温度350℃，金型温度110℃の条件で厚さ1.2mm，直径120mmの円板に成形したのち複屈折と透過率を測定した。更にこの成形板にアルミニウムを蒸着し更にウレタン樹脂を塗布して湿熱処理をおこない、外観の変化を発生したピンホールの数で評価した。

結果を第1表に示した。

（実施例4～5）

平均分子量17,100のポリカーボネート樹脂粉末を使用する以外は実施例2～3と同様に行ない、その結果を第1表に示した。

（比較例1，2）

有機ホスホナイトの配合量を変えたほかは、実施例1と同様に操作した。結果は第1表に示した。

（比較例3）

押出機のベントの吸引を行なわなかつたほかは、実施例2と同様に操作した。結果は第1表に示した。

（比較例4）

有機ホスホナイトをトリフエニルホスファイトに替えたほかは、実施例2と同様に操作した。結果は第1表に示した。

（実施例6）

ステアリン酸モノグリセライド0.04重量%を有機ホスホナイトと一緒に配合したほかは、実施例1と同様に操作した。

ペレットの平均分子量は14,800，塩素含有量は0.0014重量%，成形円板の透過率は91%，複屈折は6nmで蒸着した円板のピンホールはなく、湿熱処理後にも観察されなかつた。

第1表

	平均分子量	塩素含有量（重量%）	有機ホスホナイト 種類	有機ホスホナイト 配合量（重量%）	成形円板 透過率（%）	成形円板 複屈折（nm）	蒸着した円板のピンホールの数 処理前	蒸着した円板のピンホールの数 処理後
実施例1	14,800	0.0018	A	0.0020	91	9	0	0
〃 2	14,900	0.0012	〃	0.0045	91	6	0	0
〃 3	14,800	0.0016	B	0.0040	91	8	0	0
〃 4	17,000	0.0017	A	0.0045	90	15	0	0
〃 5	〃	0.0014	B	0.0040	90	17	0	0
比較例1	14,800	0.0013	—	—	黄褐色に着色		—	—
〃 2	14,700	0.0015	A	0.0200	90	10	0	33
〃 3	14,800	0.0130	〃	0.0045	86	20	0	15
〃 4	〃	0.0015	C	0.0048	91	7	0	41

A：テトラキス（2,4-ジターシヤリブチルフエニル）4,4'-ビフエニレンジホスホナイト
B：フエニル-（2,4,6-トリメチルフエニル）ベンゼンホスホナイト　C：トリフエニルホスファイト

特許出願人　帝人化成株式会社
代理人　弁理士　前田純博

手続補正書

昭和61年 1月 9日

特許庁長官 殿

1. 事件の表示

特願昭 60 − 189899 号

2. 発明の名称

光学用成形品

3. 補正をする者
事件との関係 特許出願人
東京都港区西新橋1−6−21
帝人化成株式会社株
代表者 山 崎 芳 樹

4. 代 理 人
東京都千代田区内幸町2丁目1番1号
(飯 野 ビ ル)
帝 人 株 式 会 社内
(7726) 弁理士 前 田 純 博
連絡先 (506) 4481

5. 補正の対象
明細書の「発明の詳細な説明」の欄

6. 補正の内容

(1) 明細書の第1頁下から第6行に「光度に」とあるを「高度に」に訂正する。

(2) 同第4頁下から第3行に「2, 2′ −」とあるを「2,2 −」に訂正する。

以 上

手続補正書

昭和61年 3月 4日

特許庁長官殿

1. 事件の表示

特願昭 60 − 189899 号

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東京都港区西新橋1−6−21
帝人化成株式会社
代表者 山 崎 芳 樹

4. 代 理 人
東京都千代田区内幸町2丁目1番1号
(飯 野 ビ ル)
帝 人 株 式 会 社内
(7726) 弁理士 前 田 純 博
連絡先 (506) 4481

5. 補正の対象
明細書の「発明の詳細な説明」の欄

6. 補正の内容
明細書の第13頁第16行に「30mm周辺部に向って」とあるを「周辺部に向って30mmの位置で」に訂正する。

以 上

a/e

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 November 2002 (14.11.2002)

PCT

(10) International Publication Number
WO 02/090085 A1

(51) International Patent Classification⁷: B29C 45/50

(21) International Application Number: PCT/US02/14154

(22) International Filing Date: 6 May 2002 (06.05.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/288,717 4 May 2001 (04.05.2001) US

(71) Applicant (*for all designated States except US*): **TREXEL, INC.** [US/US]; 45 Sixth Road, Woburn, MA 01801 (US).

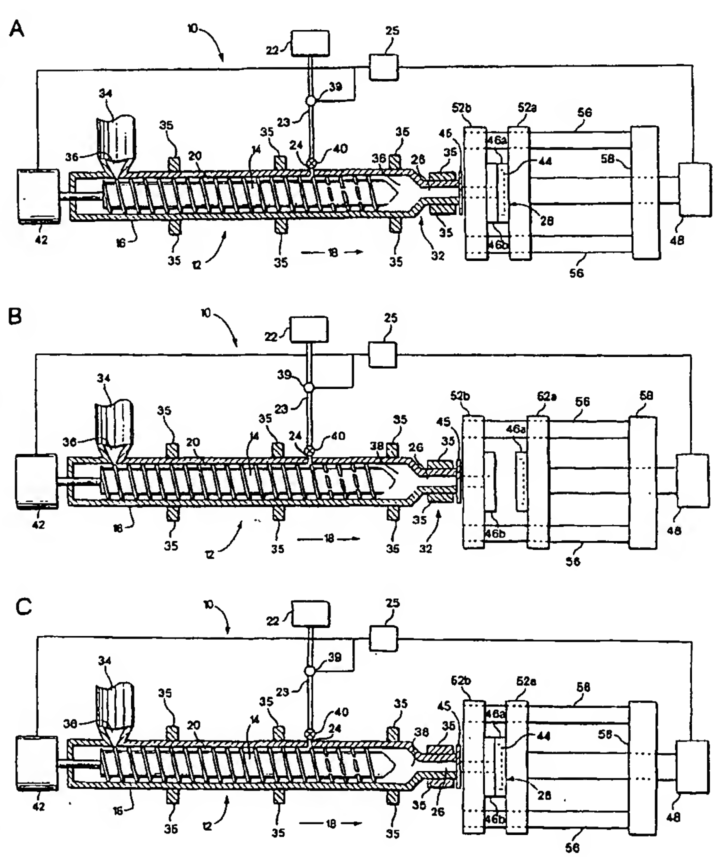
(72) Inventors; and
(75) Inventors/Applicants (*for US only*): **PIERICK, David, E.** [US/US]; 17935 Toltec Court, San Diego, CA 92127 (US). **KISHBAUGH, Levi, A.** [US/US]; 4 Kings Way, Groveland, MA 01834 (US). **XU, Jingyi** [US/US]; 204 Nashua Road, Billerca, MA 01862 (US). **CARDONA, Juan, C.** [US/US]; 62 Butman Road, Lowell, MA 01852 (US). **SHETH, Himanshu, R.** [US/US]; 44 Bucklin Road, North Andover, MA 01845 (US). **LEVESQUE, Kevin, J.** [US/US]; 18 Avon Street, Andover, MA 01810 (US). **NG, Jeffrey, L.** [US/US]; 13 Blackthorne Road, Framingham, MA 01701 (US). **KIM, Roland, Y.** [US/US]; 25 Fairfax Street, Apartment 2, Somerville, MA 02144 (US).

(74) Agent: **WALAT, Robert, H.**; Wolf, Greenfield & Sacks, P.C., 600 Atlantic Avenue, Boston, MA 02210 (US).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,

[Continued on next page]

(54) Title: INJECTION MOLDING SYSTEMS AND METHODS



(57) **Abstract:** Systems and methods for injection molding polymeric materials are provided. The systems and methods use a supercritical fluid additive. In some cases, the use of supercritical fluid additive enables formation of molded articles with low clamping forces and/or low injection pressures. Low clamping forces and/or low injection pressures may reduce the cost of a system designed to form a particular molded article. In some embodiments, the systems may include a control system that controls the operation of one or more components of the system (e.g., the extruder or the supercritical fluid additive introduction system). The systems and methods are suitable for forming polymeric foam articles including microcellular material articles.

WO 02/090085 A1

LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) **Designated States** *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

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INJECTION MOLDING SYSTEMS AND METHODS

Related Applications

This application claims priority to U.S. provisional patent application serial no. 60/288,717, filed May 5/04/01, entitled "Injection Molding Systems and Methods", the disclosure of which is incorporated herein by reference.

Field of Invention

The invention relates generally to polymer processing and, more particularly, to injection molding systems and methods used to process polymeric materials using a supercritical fluid additive.

Background of Invention

Polymeric materials may be processed to form articles having a number of different shapes and sizes. Conventional polymer processing techniques include injection molding, extrusion, and blow molding. Injection molding techniques generally involve forming a fluid stream of polymeric material in an extruder, injecting the fluid polymeric material into a mold cavity defined between mold halves, cooling the fluid polymeric material to form a molded article, and opening the mold halves to remove the article.

Injection molding systems are designed, in part, to be compatible with the molding process. For example, molding systems are designed to be compatible with the high pressures that exist within the extruder barrel and in the mold, when polymeric material is injected into the mold. In particular, molding systems are designed to provide a sufficient clamping force that holds the mold halves together during polymeric injection. Generally, at least a minimum clamping force is needed (for a given article or mold cavity) to form high quality molded articles. Clamping the mold with a low force, for example, can result in flashing of polymeric material between mold halves. Injection molding systems are also designed to provide a sufficient injection pressure to inject polymeric material into the mold cavity. Generally, at least a minimum injection pressure is needed to fill the mold cavity in a way that forms high quality molded articles.

The cost of an injection molding system depends, in part, on the design of its components. Generally the cost of a particular system increases as the clamping force

requirements increase and/or the injection pressure requirements increase. To provide a higher clamping force, for example, a larger, more expensive clamping device is required which has a higher flow rate hydraulic system. Similarly, to provide a higher injection pressure, a larger, more expensive injection device is required. To reduce cost, therefore, it is desirable to reduce the clamping force requirement and/or injection pressure requirement of a system to form a molded article.

Summary of Invention

The invention provides systems and methods for injection molding polymeric materials.

In one aspect, the invention provides a system for injection molding polymeric material. The system includes an extruder including a screw rotatable within a barrel to convey polymeric material in the direction of an outlet of the extruder. The barrel has a port formed therein connectable to a source of supercritical fluid additive. The system further includes a clamping device constructed and arranged to clamp a mold that defines a cavity connectable to the outlet of the extruder. The clamping device is capable of providing a maximum clamping force of no greater than about 80% the minimum clamping force necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

In another aspect, the invention provides a system for injection molding polymeric material. The system includes an extruder including a screw rotatable within a barrel to convey polymeric material in the direction of an outlet of the extruder. The barrel has a port formed therein connectable to a source of supercritical fluid additive. The system further includes a mold including a mold surface that defines, in part, a cavity connected to the outlet of the extruder. The mold surface that defines, in part, the cavity has a mold surface area. The system further includes a clamping device constructed and arranged to clamp the mold with a clamping force necessary to form a molded article. The ratio of the clamping force to the mold surface area is less than about 1500 lbs/in^2.

In another aspect, the invention provides a system for injection molding polymeric material. The system includes an extruder including a screw rotatable within a barrel to convey polymeric material in the direction of an outlet of the extruder. The

barrel having a port formed therein connectable to a source of supercritical fluid additive. The system further includes a clamping device constructed and arranged to clamp a first mold half and a second mold half together with a clamping force. The first and second mold halves, when clamped together, define a cavity connected to the outlet of the extruder. The system further including a first platen attachable to the first mold half, and a second platen attachable to the second mold half. The first and the second platens have a work surface area at least 10% greater than the work surface area of platens usable to form an article from polymeric material free of a supercritical fluid additive within the cavity clamped with the clamping force.

In another aspect, the invention provides a system for injection molding polymeric material. The system includes an extruder including a screw rotatable within a barrel to convey polymeric material in the direction of an outlet of the extruder. The barrel having a port formed therein connectable to a source of supercritical fluid additive. The system further includes an injection device constructed and arranged to move the screw in an axial direction within the barrel to inject a mixture of polymeric material and supercritical fluid additive into a cavity of a mold connected to the outlet of the extruder. The injection device is capable of providing an injection pressure of no greater than about 80% the injection pressure necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

In another aspect, the invention provides a system for injection molding polymeric material. The system includes an extruder including a screw rotatable within a barrel to convey polymeric material in the direction of an outlet of the extruder. The barrel has a port formed therein connectable to a source of supercritical fluid additive. The system further includes an injection device constructed and arranged to move the screw in an axial direction within the barrel to inject a mixture of polymeric material and supercritical fluid additive into a cavity of a mold connected to the outlet of the extruder. The injection device is capable of providing an injection pressure of no greater than about 80% the injection pressure necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity. The system further includes a clamping device constructed and arranged to clamp the mold. The clamping device is capable of providing a maximum clamping force of no greater than about 80% the

minimum clamping force necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

In another aspect, the invention provides a system for processing polymeric material. The system includes an extruder including a screw rotatable within a barrel to convey polymeric material in the direction of an outlet of the extruder, the barrel having a port formed therein. The system further includes a supercritical fluid additive introduction system having an inlet connectable to a supercritical fluid additive source and an outlet connectable to the port. The introduction system is directly mounted to the system.

In another aspect, the invention provides a polymeric material processing system. The system includes an extruder including a screw rotatable within a barrel to convey polymeric material in the direction of an outlet of the extruder. The barrel has a port formed therein. The system further includes a supercritical fluid additive introduction system having an inlet connectable to a supercritical fluid additive source and an outlet connectable to the port. The system further includes a control system. The control system is designed to receive inputs from the extruder and the supercritical fluid additive introduction system, and is designed to send outputs to the extruder and the supercritical fluid additive introduction system to control, in part, operation of the extruder and the supercritical fluid additive introduction system.

In another aspect, the invention provides a method for forming a molded article. The method includes providing a polymeric material molding system including an extruder and a mold, the system constructed and arranged to deliver polymeric material free of supercritical fluid additive from the extruder into the mold and forming an injection molded article using a first minimum clamping force. The method further includes delivering polymeric material admixed with a supercritical fluid additive from the extruder into the mold, and forming the injection molded article using a second minimum clamping force less than about 80% the first minimum clamping force.

In another aspect, the invention provides a method for forming a molded article. The method includes introducing a polymeric material and supercritical fluid additive mixture into a mold. The method further includes clamping the mold with a clamping force of less than about 80% of the minimum clamping force required to form a molded

article from the polymeric material free of the supercritical fluid additive, and forming a molded article.

Other advantages, aspects, and features of the invention will become apparent from the following detailed description of the invention when considered in conjunction with the accompanying drawings.

Brief Description of Drawings

Figs. 1A to 1C show an injection molding system according to one embodiment of the present invention at different stages during the molding cycle.

Figs. 2A and 2B are exploded views of the injection mold and the clamping device of the injection molding system according to one embodiment of the present invention.

Fig. 3 illustrates the mold surface area and mold wall thickness of a mold used in the injection molding system according to one embodiment of the invention.

Figs. 4A and 4B respectively illustrate the work surface area and the thickness of a platen used in the injection molding system according to one embodiment of the invention.

Fig. 5 illustrates a supercritical fluid additive introduction system directly mounted to the injection molding system according to another embodiment of the invention.

Detailed Description of Invention

Systems and methods for injection molding polymeric materials are provided. The systems and methods use a supercritical fluid additive. In some cases, the use of supercritical fluid additive enables formation of molded articles with low clamping forces and/or low injection pressures. Low clamping forces and/or low injection pressures may reduce the cost of a system as compared to conventional systems designed to form a particular molded article. In some embodiments, the systems may include a control system that controls the operation of one or more components of the system (e.g., the extruder or the supercritical fluid additive introduction system). The systems and methods are suitable for forming polymeric foam articles including microcellular material articles.

As used herein, the term "clamping force" refers to the force that holds together the two mold halves which define the mold cavity. The clamping force can be determined, for example, by multiplying the hydraulic pressure by the piston surface area in a clamping device (for hydraulic clamping devices); or, by measuring the force using a load cell associated with the mold halves and/or platens; or, by measuring tie bar elongation or strain and converting to a clamping force.

As used herein, the term "injection pressure" refers to the pressure at which polymeric material is injected into the mold. The injection pressure can be determined, for example, by measuring the hydraulic load (for hydraulic injection systems), or by measuring the servomotor torque and multiplying it by the appropriate mechanical advantage factor of the system (for electrical injection systems).

As used herein, the term "supercritical fluid additive" refers to any additive that is a supercritical fluid under temperature and pressure conditions within an extruder (12, Fig. 1) of an injection molding system. It should be understood that the supercritical fluid additive may or may not be a supercritical fluid prior to introduction into the extruder (e.g., when supercritical fluid additive is in source 22, Fig. 1) and that the additive may be introduced into the polymeric material in the extruder in any flowable state, for example, as a gas, liquid, or supercritical fluid.

Figs. 1A-1C schematically illustrate an injection molding system 10 according to one embodiment of the present invention. An extruder 12 of molding system 10 includes a polymer processing screw 14 that is rotatable within a barrel 16 to convey polymeric material in a downstream direction 18 within a polymer processing space 20 defined between the screw and the barrel. The system includes a supercritical fluid additive introduction system 21 for introducing the supercritical fluid additive into the polymeric material thereby forming a mixture of polymeric material and supercritical fluid additive in polymer processing space 20. Supercritical fluid additive introduction system 21 includes a source 22 of supercritical fluid additive that is connected via conduit 23 to a port 24 formed within the barrel. Extruder 12 includes an outlet 26 connected to an injection mold 28. Optionally, system 10 includes a control system 25 that is capable of controlling the injection molding process and/or supercritical fluid additive introduction into the polymeric material. The supercritical fluid additive lowers the viscosity of the

mixture which permits forming molded articles using low clamping forces and/or low injection pressures, as described further below.

Generally, injection molding system 10 operates cyclically to produce multiple molded articles. At the beginning of a typical molding cycle, screw 14 is positioned at a downstream end 32 of barrel 16. Polymeric material, typically in pelletized form, feeds into polymer processing space 20 from a hopper 34 through an orifice 36. Barrel 16 may be heated by one or more heating units 35. Screw 14 rotates to plasticate polymeric material and to convey the polymeric material in downstream direction 18. Polymeric material is generally in a fluid state at the point of supercritical fluid additive introduction. The flow rate of supercritical fluid additive into the polymeric material may be metered, for example, by a metering device 39 positioned between source 22 and port 24. As described further below, metering device 39 may also be connected to control system 25 which sends signals to control supercritical fluid additive flow rate. The mixture of polymeric material and supercritical fluid additive is conveyed downstream by the rotating screw and accumulated in a region 38 (Fig. 1B) within the barrel downstream of the screw. The accumulation of the mixture in region 38 creates a pressure that forces the screw axially in an upstream direction in the barrel. After a sufficient charge of the mixture has been accumulated, screw 14 ceases to rotate (which stops the plastication of polymeric material) and stops moving in the upstream direction (Fig. 1C). Preferably, when the screw no longer plasticates polymeric material the introduction of supercritical fluid additive into the polymeric material is, or has been, stopped, for example, by the operation of an injector valve 40 associated with port 24.

Then, the screw is moved axially in a downstream direction by an injection device 42 to downstream end 32 of the barrel, returning to the screw position in Fig. 1A, to inject the accumulated charge of the mixture through outlet 26 of the extruder and into a cavity 44 defined between mold halves 46a, 46b via a passageway 47. A shut-off nozzle valve 45 associated with the outlet of the extruder typically is opened to permit the mixture to flow into the cavity. After the charge is injected into the cavity, valve 45 is typically closed. As described further below and shown in Figs. 2A and 2B, a clamping device 48 holds mold halves 46a, 46b of the mold together during injection and the subsequent cooling of the polymeric material. After the polymeric material sufficiently solidifies, clamping device 48 separates mold halves 46a, 46b to open mold

28 and to eject a molded article. In the illustrative embodiment, mold 28 is opened during the accumulation of the mixture of polymeric material and blowing agent in region 38 downstream of screw 14 (Fig. 1B). The molding cycle is repeated to produce additional molded articles.

It should be understood that molding system 10 may include a number of variations from the illustrative embodiment as known to one of ordinary skill in the art. For example, mold 28 may define more than one cavity in which articles may be molded and may include a hot runner gate to introduce polymeric material into the cavities. The hot runner gate may also be provided with a valve to selectively control introduction of the polymeric material. It should also be understood that the injection molding system may be a hydraulic system, an electrical system, or a hybrid hydraulic/electric system.

Control system 25, when provided, may receive input signals from and send output signals to one or more components of the injection molding system. The control system may also receive manual input signals in response to entries by an operator. In particular, control system 25 may be used to synchronize the operation of the injection molding system and supercritical fluid additive introduction. For example, control system 25 can coordinate the operation of metering device 39 with screw 14 so that a desired amount of supercritical fluid additive is introduced into the polymeric material to form a mixture having the desired weight percentage of supercritical fluid additive, as described further below. In some embodiments, a first controller controls the operation of the injection molding system and a second controller controls supercritical fluid additive introduction. In other embodiments, a single controller controls operation of the injection molding system and supercritical fluid additive introduction. The operation of the control system is described further below. Suitable control systems have been further described in commonly-owned, co-pending U.S. Patent Application Serial No. (not yet assigned), entitled "Method and Apparatus for Controlling Foam Molding Processing", by Kim et. al., filed on April 5, 2001, which is incorporated herein by reference.

Referring to Figs. 2A and 2B, injection mold 28 and clamping device 48 are shown according to one embodiment of injection molding system 10. In the illustrative embodiment, mold half 46a is secured to a movable platen 52a, and mold half 46b is secured to a fixed platen 52b. Platen 52a is slidably mounted on a plurality of tie bars 56 which extend from a backside 58 of system 10 to fixed platen 52b. Platen 52a

reciprocates on tie bars 56 to open and close mold 28 in response to the action of clamping device 48 which is synchronized with the molding cycle. Mold 28 is closed when clamping device 48 pushes platen 52a in the direction of arrow 60 which forces mold half 46a against mold half 46b (Fig. 2A). As described above, clamping device 48 holds mold halves 46a, 46b together with a clamping force during injection and while the polymeric material cools. To open the mold, clamping device retracts platen 52a in a direction opposite arrow 60 which separates mold halves 46a, 46b (Fig. 2B).

It should be understood that other configurations of the injection mold and clamping device may also be used in connection with the systems and methods of the invention. For example, in some cases, systems and methods of the invention may not include platens. In these cases, the movable mold half may be secured directly to the clamping device and the other mold half secured to the frame of the system. Eliminating platens from the system can result in large cost savings. In other embodiments, a pressure measuring device may be associated with mold cavity 44 to monitor pressure within the mold (i.e., cavitation pressure). The pressure measuring device may, for example, access the mold cavity through a wall of one of the mold halves. The pressure measuring device can send output signals representative of the cavitation pressure, for example, to control system 25 to control various molding parameters such as injection speed and injection force, amongst others.

Clamping device 48 may be any suitable type. Clamping device 48 may be hydraulically or mechanically/electrically powered. A clamping device can be characterized by the maximum force it is capable of providing. Suitable clamping devices may provide a maximum force, for example, of between about 10 tons and about 10,000 tons, and more typically between about 30 tons and about 3,000 tons. The specific clamping force depends upon the article being molded amongst other factors. Generally, the cost of a clamping devices is proportional to the maximum force it can apply (i.e., the greater the maximum force, the greater the cost).

Clamping device 48 generally needs to provide a minimum clamping force to form a high quality molded article. Thus, clamping device 48 is capable of providing a maximum force greater than the minimum force required to form the desired article. The minimum clamping force, for example, is defined as the clamping force sufficient to prevent polymeric material injected into cavity 44 from flashing between mold halves

46a, 46b. The minimum clamping force required depends upon several factors including the cavity shape and cavity dimensions used to form the article.

As described above, the addition of the supercritical fluid additive can lower the minimum clamping force required to form a molded article. The lowering of the clamping force results from the ability of the supercritical fluid additive to reduce the viscosity of the polymeric material which leads to lower cavitation pressures (i.e., the pressure of polymeric material within mold cavity 44). The invention includes the realization that processing with the supercritical fluid additive to form a molded article permits using clamping devices that provide lower maximum forces than the minimum force necessary to form the article when processing without the supercritical fluid additive. The reduction in required clamping force depends, in part, upon the amount of supercritical fluid additive in the mixture. In some embodiments, system 10 forms a molded article from the polymeric material and supercritical fluid additive mixture using clamping device 48 which provides a maximum clamping force of less than about 80% the minimum clamping force necessary to form the same article from polymeric material free of a supercritical fluid additive. In this context, the article formed from polymeric material free of supercritical fluid additive has substantially the same quality, external appearance, dimensions and polymeric composition as the article formed using the mixture of polymeric material and supercritical fluid additive. However, in some cases, the article formed using the mixture may be a polymeric foam, while the article formed using polymeric material free of supercritical fluid additive may be a solid polymer. In other embodiments, even greater reductions in clamping force can be utilized. For example, system 10 may form a molded article from the polymeric material and supercritical fluid additive mixture using clamping device 48 which provides a maximum clamping force of less than about 65%, less than about 50%, less than about 30%, or even less than about 10%, the minimum clamping force necessary to form the same article from polymeric material free of a supercritical fluid additive. The reduction in necessary clamping force enables articles to be formed using injection molding systems that may be significantly less expensive than systems used to form the same articles without the supercritical fluid additive.

The reduction in clamping force necessary to form a molded article can also be measured with respect to the mold surface area. Fig. 3 schematically illustrates the mold

surface area A of mold cavity 44 according to one embodiment of the present invention. As used herein, the term "mold surface area" is defined as the surface area of a back surface 59 (i.e., a surface generally perpendicular to the flow of polymeric material into the mold cavity) of cavity 44. The mold surface area does not include side surfaces 61 of mold cavity 44. The ratio of clamping force to mold surface area generally must be greater than a minimum value to ensure the formation of high quality molded articles. Generally, conventional molding systems and methods use clamping force to mold surface area ratios of greater than about 2000 lbs/in^2. In systems and methods of the invention, lower ratios may be utilized. For example, the systems and methods of the invention can have ratios of clamping force to mold surface area of less than about 1500 lbs/in^2. In other cases, the ratio of clamping force to mold surface area is less than about 1000 lbs/in^2. Even lower ratios of less than about 750 lbs/in^2, or less than about 500 lbs/in^2 may also be used. Ratios may be decreased, for example, by increasing the amount of the supercritical fluid additive in the mixture. In some cases, lower ratios may be desired because they are indicative of greater cost savings associated with clamping device 48 and, in turn, injection molding system 10.

The supercritical fluid additive also permits using platens 52a, 52b that have large work surface areas. As used herein, the term "work surface area" of a platen refers to the surface area on a platen to which a mold half can be secured. Fig. 4A illustrates a work surface area A′ of platens 52a, 52b. The work surface area generally includes the entire surface area of the platen but does not include holes 63 formed in the platens through which tie bars 56 extend (Fig. 2A-2B). Generally, the work surface area of a platen is limited to a maximum value for a fixed clamping force. Using platens with too large work surface areas for a fixed clamping force can result in the formation of unsatisfactory molded articles, in part, due to flashing of polymeric material between mold halves. In particular, platens of systems and methods of the invention may have work surface areas that are greater than the work surface areas of platens (for a fixed clamping force) used in conventional systems and methods that do not utilize supercritical fluid additives. Larger work surface area platens may be used, in part, because the work space between tie bars can be increased and/or tie bar diameter can be decreased.

In some cases, the systems and methods may use platens having at least about 10% greater work surface areas for a fixed clamping force than platens used in systems and methods that do not use supercritical fluid additives. In some cases, the systems and methods may use platens having at least about 30% greater work surface area, or even at least about 50% greater work surface area, for a fixed clamping force than platens used in systems and methods that do not use supercritical fluid additives. Increasing the work surface area of the platen enables mold cavities with larger areas to be used and, thus, permits molding of articles with larger areas. The amount of increase in work surface area depends, in part, on the amount of supercritical fluid additive in the mixture.

The supercritical fluid additive also permits using the systems and methods of the invention with platens that are relatively thin and/or less rigid. Thin or less rigid platens can be used because of the reduction in cavitation pressure. Fig. 4B illustrates a thickness t of platen 52a. In particular, platens 52a, 52b may be made thinner than platens used to form the same article without the supercritical fluid additive at a fixed clamping force. For example, platens 52a, 52b may be made greater than about 10% thinner, or even greater than about 20% thinner, than platens used to form the same molded article without the supercritical fluid additive at a fixed clamping force. Decreasing platen thickness can reduce the mass of the platen which permits using smaller and lighter actuators and/or a smaller (i.e., capable of supporting less weight) frame which supports the clamping device. The reduced mass also allows the platen to be moved more rapidly by a given force and, thus, allows for shorter cycle times.

The supercritical fluid additive also permits using mold halves 46a, 46b that have relatively thin walls 62 (Fig. 3). Thin walls 62 can be used because of the reduction to cavitation pressure. In particular, mold walls 62 may be made thinner than mold walls used to form a given article without the supercritical fluid additive at a fixed clamping force. For example, mold walls 62 may be made greater than about 10% thinner, or even greater than about 20% thinner, than mold walls used to form a given molded article without the supercritical fluid additive at a fixed clamping force. Thinner mold walls enhance the ability of a mold to be cooled, for example via water cooling, which can lead to shorter cycle times and increased productivity.

Using the supercritical fluid additive also may enable forming mold halves 46a, 46b of less expensive materials than used in certain conventional systems that do not

utilize the supercritical fluid additive. Typically, mold halves 46a, 46b are formed of relatively expensive high strength steels to withstand high cavitation pressures and to have long usable lives. Because cavitation pressures are lowered in the systems and methods of the invention, in some cases, mold halves 46a, 46b may be formed of materials that are not as strong (and expensive) as high strength steel, such as aluminum. Such mold halves 46a, 46b can provide similar performance using less expensive material. Mold halves 46a, 46b made of aluminum are more easily machined and also may be cooled quickly more quickly than steel due to the high thermal conductivity of aluminum. Therefore, cycle times may be reduced when using aluminum mold halves 46a, 46b which can increase productivity.

The supercritical fluid additive can also result in lower injection pressures than conventional systems and methods which do not utilize the supercritical fluid additive. The lower injection pressures can be achievable because the supercritical fluid additive reduces the viscosity of the polymeric material. When injection velocity is held substantially constant, typical injection pressures in the systems and methods of the present invention are between about 500 psi and about 10,000 psi, while conventional systems and methods which do not utilize the supercritical fluid additive are between about 5,000 psi and about 30,000 psi. The specific injection pressure depends on a variety of factors including material type, processing conditions, and dimensions of extruder outlet 26 and mold cavity 44. In some embodiments, systems 10 can form a molded article by injecting a mixture of polymeric material and supercritical fluid additive into cavity 44 at an injection pressure of less than about 80% the injection pressure necessary to form the same article from polymeric material free of a supercritical fluid additive. In other embodiments, even greater reductions in injection pressure can be achieved. For example, system 10 can form a molded article by injecting a mixture of polymeric material and supercritical fluid additive into cavity 44 at an injection pressure of less than about 65%, or even less than about 50%, the injection pressure necessary to form the same article from polymeric material free of a supercritical fluid additive. The amount that the injection pressure is lowered depends, in part, on the amount of supercritical fluid additive present in the mixture. The lower injection pressures may also enable increased injection velocity which can improve cycle time and process performance.

Lower injection pressures permit using injection devices 42 that provide lower maximum injection force. The cost of injection device 42 generally decreases as the maximum injection force required is reduced. Thus, system 10 may be less expensive when designed to form the same molded article than conventional systems which do not utilize the supercritical fluid additive.

Lower injection pressures also may enable barrel 16 to be made thinner than in conventional systems which do not utilize the supercritical fluid additive. The strength of barrel 16 depends, in part, on its thickness. Generally, a barrel is designed to withstand the peak pressure (e.g., the injection pressure) experienced in the extruder. Thus, reduced injection pressures permit use of a thinner barrel 16 in system 10. Thinner barrels are generally less expensive, thus, resulting in cost savings associated with the systems of the present invention. Also, as a result of the lower injection pressure, it may be possible to drill water channels directly into barrel 16. Such water channels can efficiently cool the polymeric material which is advantageous in certain processes.

Screw 14 may be designed to have a large diameter as a result of the lower injection pressures. For example, screw 14 may be made greater than about 40% larger than the cross-sectional area of a screw used to form a given molded article without the supercritical fluid additive at a fixed clamping force. Larger screw cross-sectional areas enable the faster production of larger shot sizes and larger molded parts by injecting more material into the mold at a quicker rate and allowing faster recovery rates to decrease cycle time.

The lower clamping forces and lower injection pressures may allow systems of the invention to use less power than conventional systems that do not utilize the supercritical fluid additive. Savings in power usage can result in considerable cost savings.

In certain preferred embodiments, the supercritical fluid additive may function as a physical blowing agent which forms cell within the polymeric material article. Typically, the supercritical fluid additive forms the cell via a nucleation step as a result of the pressure drop that occurs when the mixture is injected into mold 28 through outlet 26 of extruder 12. Thus, the systems and methods of the invention can produce polymeric foam articles, including microcellular materials, as described further below. In particular, the systems and methods of the invention may be designed to form

microcellular polymeric articles as described in International Publication No. WO 98/31521 (Pierick et. al.) which is incorporated herein by reference. However, in other cases, the systems and methods of the invention may form solid polymeric articles without any cells. In these cases, the supercritical fluid additive functions as a viscosity lowering aid, but not as a blowing agent that nucleates and grow cells.

The supercritical fluid additive may have a variety of compositions including nitrogen, carbon dioxide, and mixtures thereof. According to one preferred embodiment, the supercritical fluid additive is carbon dioxide. In another preferred embodiment the supercritical fluid additive is nitrogen. In certain embodiments, the supercritical fluid additive is solely carbon dioxide or nitrogen. In embodiments in which supercritical fluid additive is nitrogen, source 22 may be a nitrogen generator which produces nitrogen from the atmosphere.

As described above, the supercritical fluid additive may be introduced into the polymeric material to provide a mixture having the desired weight percentage. For example, metering device 39 may be used in conjunction with control system 25 to provide the desired percentage. The desired weight percentage of supercritical fluid additive may depend upon a number of factors including the extent of viscosity reduction. Generally, increasing the weight percentage of the supercritical fluid additive in a mixture will further decrease the viscosity. However, increasing the weight percentage of the supercritical fluid additive may have other processing effects such as resulting in process instability, amongst others. The supercritical fluid additive percentage is typically less than about 10% by weight of the mixture of polymeric material and supercritical fluid additive. In some embodiments, the supercritical fluid additive level is less than about 5%. In many cases, it may be preferable to use low weight percentages of supercritical fluid additive. For example, the supercritical fluid additive level may be less than about 3%, in others less than about 1%, and still others less than about 0.1% by weight of polymeric material and supercritical fluid additive mixture. The supercritical fluid additive level may also depend upon the type of supercritical fluid additive used. For example, to achieve the same reduction in viscosity, carbon dioxide typically has to be added at greater amounts than nitrogen.

The supercritical fluid additive introduction rate may be coupled, for example by control system 25, to the flow rate of polymeric material to produce a mixture having the

desired weight percentage. Supercritical fluid additive may be introduced into the polymeric material over a wide range of flow rates. In some embodiments, the supercritical fluid mass flow rate into the polymeric material may be between about 0.001 lbs/hr and about 100 lbs/hr, in some cases between about 0.002 lbs/hr and about 60 lbs/hr, and in some cases between about 0.02 lbs/hr and about 10 lbs/hr.

In some embodiments, the system includes a bypass valve positioned between source 22 and port 24. When the bypass valve is in one configuration, the flow of blowing agent from the source to the port is diverted through the bypass valve and, optionally, a bypass passageway connected to the outlet of the valve. The blowing agent may be, for example, diverted through the bypass valve and released to the atmosphere or re-introduced to source 22. When the bypass valve is in a second configuration, blowing agent may flow from the source to the port. Suitable bypass valve designs and arrangements have been described in co-pending, commonly-owned, U.S. application serial no. 09/782,673, filed February 13, 2001, entitled "Blowing Agent Delivery System", which is incorporated herein by reference. The presence of a bypass valve may be particularly useful when it is desired to have constant blowing agent flow from the source, for example, to increase the stability of blowing agent flow. In some embodiments, the bypass valve may be combined with injector valve 40 in a single device. In other embodiments, the bypass valve may be a separate device than the injector valve.

In some embodiments, particularly when forming microcellular materials, it may be preferable to form a single-phase solution of polymeric material and supercritical fluid additive within polymer processing space 20. That is, the mixture of polymeric material and supercritical fluid additive is a single-phase solution. In certain embodiments, it may be preferable to maintain the single-phase condition until the solution is injected into mold 28. To aid in the formation of a single-phase solution, supercritical fluid introduction may be done through a plurality of ports 24 arranged in the barrel, though it should be understood that a single port may also be utilized to form a single-phase solution. When multiple ports 24 are utilized, the ports can be arranged radially about the barrel or in a linear fashion along the axial length of the barrel. An arrangement of ports along the length of the barrel can facilitate injection of supercritical fluid additive at a relatively constant location relative to the screw when the screw moves axially (in an

upstream direction) within the barrel as the mixture of polymeric material and supercritical fluid additive is accumulated. Where radially-arranged ports are used, ports 24 may be placed at the 12:00 o'clock, 3:00 o'clock, 6:00 o'clock and 9:00 o'clock positions about the extruder barrel, or in any other configuration as desired. Port 24 may include a single orifice or a plurality of orifices. In the multi-orifice embodiments (not illustrated), the port may include at least about 2, and some cases at least about 4, and others at least about 10, and others at least about 40, and others at least about 100, and others at least about 300, and others at least about 500, and in still others at least about 700 orifices. In another embodiment, port 24 includes an orifice containing a porous material that permits supercritical fluid additive to flow therethrough and into the barrel, without the need to machine a plurality of individual orifices. Suitable port arrangements and designs (including multi-hole orifice designs) are further described in International Publication No. WO 98/31521 (Pierick et. al.), which is referenced above.

To further promote the formation of a single-phase solution, port 24 may be located at a section of the screw that may include full, unbroken flight paths. In this manner, each flight, passes or "wipes" the port including orifices periodically, when the screw is rotating. This wiping increases rapid mixing of supercritical fluid additive and polymeric material in the extruder and the result is a distribution of relatively finely divided, isolated regions of supercritical fluid additive in the polymeric material immediately upon injection into the barrel and prior to any mixing. Downstream of port 24, the screw may include a mixing section which has highly broken flights to further mix the polymeric material and supercritical fluid additive mixture to promote formation of a single-phase solution.

As described above, control system 25 may receive input signals from and send output signals to different components of the injection molding system including components of the extruder, components of the supercritical fluid introduction system, or components of the injection mold. The inputs may be indicative of different processing or equipment conditions. For example, the inputs may be indicative of the configuration of shut-off nozzle valve 45, the axial position of screw 14 within the barrel, the configuration of injector valve 40, the pressure of polymeric material within the barrel, the pressure of polymeric material accumulated in a region within the barrel downstream of the screw, the mass of supercritical fluid additive introduced into the polymeric

material, the delivery pressure of supercritical fluid additive introduced into the polymeric material, and the rotational speed of the screw. It should be understood that other inputs are also possible including inputs of additional processing or equipment conditions. Other suitable controller inputs have also been described in U.S. patent application serial no. (not yet assigned), entitled "Method and Apparatus for Controlling Foam Molding Processing", by Kim et. al., filed on April 5, 2001, and incorporated by reference above. The components which send inputs to the control system may be measuring devices (e.g., pressure transducers, and melt or metal thermacouples), or operative devices, themselves (e.g., valves and regulators). The inputs may be used to monitor certain processing or equipment conditions, and/or may be used, at least in part, to determine outputs sent by the control system to control processing or equipment conditions.

In some cases, the operator provides one or more inputs to the control system. The operator may provide an input causing the controller to activate various aspects of process control (e.g., control of polymeric pressure within the extruder, control of injector valve configuration, and the like). In embodiments which include a first controller associated with the extruder and a second controller associated with the supercritical fluid additive system, the operator may provide an input to one of the controllers (e.g., the first controller) and have that controller send a signal to the other controller (e.g., the second controller) indicative of the input.

The output signals are sent by control system 25, for example, to control the operation of different components of the injection molding system which may provide desired processing or equipment conditions. The outputs may control, for example, the configuration of shut-off nozzle valve 45, the operation of heating unit(s) mounted on the barrel, the operation of heating unit(s) associated with the shut-off valve, the configuration of hot runner gate valve(s), the axial position of the screw, the configuration of a bypass valve, the configuration of injector valve(s) 40, the pressure of polymeric material within the barrel, the pressure of polymeric material accumulated in a region within the barrel downstream of the screw, the mass of supercritical fluid additive introduced into the polymeric material, the delivery pressure of supercritical fluid additive introduced into the polymeric material, and the rotational speed of the screw. It should be understood that other outputs are also possible including outputs that control

additional processing or equipment conditions. Other suitable controller outputs have also been described in U.S. patent application serial no. (not yet assigned), entitled "Method and Apparatus for Controlling Foam Molding Processing", by Kim et. al., filed on April 5, 2001, and incorporated by reference above.

In some cases, the control system is designed to provide an indication to a operator when certain processing or equipment conditions are present. For example, the control system may indicate to an operator when undesirable, or dangerous, processing or equipment conditions are present so that the operator may adjust conditions accordingly. The control system may alternatively, or in addition to, providing indication to the operator, send an output signal that adjusts conditions accordingly. For example, the control system may send an output to the supercritical fluid additive introduction system so that supercritical fluid additive is not introduced into the polymeric material when certain conditions are present.

The control system may provide indication to an operator and/or send an output to adjust conditions when processing conditions differ from desired conditions by a selected amount. For example, the control system may provide indication or send an output when one of the following processing conditions is present: the pressure of polymeric material within the barrel is greater or less than a desired pressure by an offset value (e.g., ±200 psi), for example, at a control system or user determined time in the molding cycle, the mass of supercritical fluid additive introduced into the polymeric material is greater or less than a desired mass by an offset value (e.g., ±10 mg), or the delivery pressure of supercritical fluid additive introduced into the polymeric material is greater or less than a desired delivery pressure by an offset value (e.g., ±50 psi), for example, at a control system or user determined time in the molding cycle. The desired condition (e.g., polymeric material pressure, mass of supercritical fluid additive, or delivery pressure) and offset value may depend upon the particular process. The desired condition and/or offset value may be selected by the operator at the beginning of the process, or may be permanently programmed into the control system.

In some cases, the control system provides an indication to an operator and/or adjusts conditions when processing conditions (e.g., polymeric material pressure, mass of supercritical fluid additive, or delivery pressure) during a molding cycle differ by a

given amount from processing conditions in the previous molding cycle, for example, at a control system or user determined time in the molding cycle.

In some cases, the control system provides an indication to an operator when the injection mold is not closed, when safety gates or doors associated with the injection molding system are open, when the desired supercritical fluid additive flow rate is out of range, when supercritical fluid additive supply is low, or when any measuring device (e.g., a thermocouple) is malfunctioning, amongst others. In addition, the control system may provide indication of any safety or operation alarm to the user.

Referring to Fig. 5, in some embodiments, an injection molding system 65 includes a supercritical fluid additive introduction system 66 directly mounted to system 65, for example, to a frame 75 of extruder 12. Introduction system 66 can include metering device 39 which, in some cases, measures and meters the supercritical fluid additive flow rate and can optionally display the flow rate on a display 68. In other cases, metering device 39 does not measure, but only meters supercritical fluid additive flow. In other cases, the supercritical fluid additive can be measured and added volumetrically to the polymeric material. Optionally, introduction system 66 also includes a pump 70 which increases the pressure of the supercritical fluid additive above that in barrel 16 to permit introduction. The pump may or may not be directly mounted to the system. Source 22, which in the illustrative embodiment is separate (i.e., not permanently mounted) from system 65, supplies the supercritical fluid additive to introduction system 66 via conduit 72. The outlet of introduction system 66 is connected to port 24. The embodiment of Fig. 5 including the directly mounted introduction system can be advantageous by eliminating components (e.g., metering device 39) external of system 65. Thus, valuable floor space may be saved by using system 65.

As described above, systems and methods of the invention can be used to form solid or polymeric foam articles. Polymeric foam articles may be produced over a wide range of void fractions. Polymeric foams may be used that have a void fraction of between about 1% and about 99%. In some embodiments, higher density foams are used having a void fraction of less than 50%, in other cases a void fraction of less than 30%, and in some cases a void fraction of between about 5% and about 30%. The particular void fraction will depend upon the application.

In certain embodiments, microcellular material may be formed. Suitable microcellular materials have been described, for example, in International Publication No. WO 98/31521 (Pierick et. al.), referenced above. Microcellular materials, or microcellular foams, have small cell sizes and high cell densities. As used herein, the term "cell density" is defined as the number of cells per cubic centimeter of original, unfoamed polymeric material. As used herein, the term "average cell size" is the numerical average of the size of the cells formed in an article. The average cell size can be determined, for example, by scanning electron microscopy (SEM) analysis of a representative area of the article.

In some embodiments, the microcellular materials have an average cell size of less than 100 microns; in other embodiments, an average cell size of less than 50 microns; in other embodiments, an average cell size of less than 25 microns; in other embodiments, an average cell size of less than 10 microns; and, in still other embodiments, an average cell size of less than 1 micron. In some of these microcellular embodiments, the cell size may be uniform, though a minority amount of cells may have a considerably larger or smaller cells size. In certain cases, foam articles (including microcellular foams) may have a non-uniform cell size. In some of cases, different regions of the article may have cells of different size. For example, edge regions of the article may generally have a smaller cell size than interior regions of the article.

In some cases, the microcellular materials have a cell density of greater than 10^6 cells/cm^3, in others greater than 10^7 cells/cm^3, in others greater than 10^8 cells/cm^3, and in others greater than 10^9 cells/cm^3.

In another set of embodiments, polymeric articles are formed that approach, but do not achieve, the requirements of microcellular material. For example, articles may have at least 70% of the total number of cells in the polymeric portion have a cell size of less than 150 microns. In some embodiments at least 80%, in other cases at least 90%, in other cases at least 95%, and in other cases at least 99% of the total number of cells have a cell size of less than 150 microns. In other embodiments, the foam portion may be provided in which at least 30% of the total number of cells have a cell size of less than 800 microns, more preferably less than 500 microns, and more preferably less than 200 microns.

Any type of injection molded article can be produced using the systems and methods of the invention. The articles may generally comprise any type of polymeric material which can be injection molded. Suitable materials include thermoplastic polymers which may be amorphous, semicrystalline, or crystalline materials. Typical examples of polymeric materials include styrenic polymers (e.g., polystyrene, ABS), polyolefins (e.g., polyethylene and polypropylene), fluoropolymers, polyamides, polyimides, polyesters, polycarbonate, polyphenylene ether (PPE), thermoplastic elastomers, vinyl halides (e.g., PVC), acrylic (e.g., PMMA) and the like. The article may also include any number of other additives known in the art such as reinforcing agents, lubricants, plasticizers, colorants, fillers and the like. Optionally, the articles may include a nucleating agent, such as talc or calcium carbonate. In many embodiments, the articles are free of a nucleating agent. The articles are generally free of residual chemical blowing agents or reaction byproducts of chemical blowing agents. The articles are also generally free of non-atmospheric blowing agents, for example, when the supercritical fluid additive is an atmospheric component (e.g., nitrogen, carbon dioxide).

The function and advantages of these and other embodiments of the present invention will be more fully understood from the examples below. The following example is intended to illustrate the benefits of the present invention but does not exemplify the full scope of the invention.

Comparative Example

An 88-ton reciprocating screw injection molding machine manufactured by Arburg, Inc. (Newington, CT) was used to mold a spout insert for a bottle. The material used to make the spout insert was high density polyethylene (Fortiflex T50-2000-119, no filler, 20 g/10 min melt flow rate) manufactured by Solvay (Houston, TX). The mold used to mold the spout insert was a single cavity mold that was defined between two mold halves. The mold included a Husky (Bolton, Ontario) valve gate hot runner system. The system also included a source of supercritical additive (nitrogen) which was connected to the barrel of the injection molding machine. A valve provided the ability to shut-off flow of the supercritical additive into the injection molding machine to simulate a system that does not include a source of supercritical fluid additive.

Bottle 1 was formed using the system with the valve configured to prevent flow of supercritical fluid additive into the injection molding machine. Bottle 2 was formed using the system with the valve configured to allow flow of supercritical fluid additive into the injection molding machine. Bottle 1 was a solid article (non-foam) and Bottle 2 was a microcellular polymeric foam. The clamping force, injection pressure, and cycle time were measured for both bottles. The weight of both bottles and the average cell size of Bottle 2 was determined. The average cell size was determined by averaging the size of the cells in a representative cross-section as determined by SEM analysis. The results of the measurements are summarized in the table below.

Measurement	BOTTLE 1	BOTTLE 2
Supercritical Fluid Additive (%)	0	0.26
Weight (g)	8.0	7.2
Void Fraction (%)	0	10
Clamping Force (tons)	50	3
Injection Pressure (psi)	2200	1370
Cycle Time (s)	11.1	9.8
Average Cell Size (micron)	no cells	50

This example illustrates the ability to reduce clamping force and injection pressure using the supercritical fluid additive according to methods and systems of the invention. The clamping force was reduced from 50 tons to 3 tons (94%) and the injection pressure was reduced from 2200 psi to 1370 psi (38%) by using the supercritical fluid additive.

Those skilled in the art would readily appreciate that all parameters listed herein are meant to be exemplary and that the actual parameters would depend upon the specific application for which the methods and articles of the invention are used. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalence thereto, the invention may be practiced otherwise than as specifically described.

The different embodiments of the invention may or may not be used in combination with one another. For example, embodiments of the invention that utilize

low clamping forces and/or low injection pressures may not utilize a control system. Also, embodiments of the invention that utilize a control system may not utilize low clamping forces and/or low injection pressures. However, it should also be understood that embodiments that utilize a control system may also utilize low clamping forces and/or injection pressures.

What is claimed is:

CLAIMS

1. A polymeric material processing system comprising:

an extruder including a screw rotatable within a barrel to convey polymeric material in the direction of an outlet of the extruder, the barrel having a port formed therein;

a supercritical fluid additive introduction system having an inlet connectable to a supercritical fluid additive source and an outlet connectable to the port; and

a control system designed to receive inputs from the extruder and the supercritical fluid additive introduction system, and designed to send outputs to the extruder and the supercritical fluid additive introduction system to control, in part, operation of the extruder and the supercritical fluid additive introduction system.

2. The system of claim 1, wherein the control system includes a single controller.

3. The system of claim 1, wherein the control system includes a first controller associated with the extruder and a second controller associated with the supercritical fluid additive introduction system.

4. The system of claim 1, further comprising a mold defining a cavity connected to the outlet of the barrel.

5. The system of claim 4, further comprising a passageway that connects the mold to the outlet of the barrel and a shut-off nozzle valve positioned in the passageway, the shut-off valve having an open configuration which permits flow of polymeric material therethrough and a closed configuration which prevents flow of polymeric material therethrough.

6. The system of claim 5, wherein the control system receives an input indicative of the configuration of the shut-off nozzle valve.

7. The system of claim 5, wherein the control system sends an output to control the configuration of the shut-off nozzle valve.

8. The system of claim 5, wherein the shut-off nozzle valve has a heating unit associated therewith and the control system sends an output to control operation of the heating unit.

9. The system of claim 4, further comprising a hot runner gate within the mold, the hot runner gate including a valve.

10. The system of claim 9, wherein the control system sends an output to control the configuration of the hot runner gate valve.

11. The system of claim 1, wherein the extruder includes heating units mounted on the barrel, the control system sending an output to control the operation of the heating units.

12. The system of claim 11, wherein the control system sends an output to control the operation of the heating units based, at least in part, on an input from the extruder.

13. The system of claim 1, wherein the control system receives an input indicative of the axial position of the screw within the barrel.

14. The system of claim 1, wherein the control system sends an output to the extruder to control the axial position of the screw within the barrel.

15. The system of claim 1, wherein a passageway connects the inlet of the supercritical fluid additive introduction system to the outlet of the supercritical fluid additive introduction system.

16. The system of claim 15, wherein a bypass valve is positioned within the passageway of the supercritical additive introduction system, the bypass valve having a

first configuration that permits flow of blowing agent from the inlet to the outlet and a second configuration that diverts flow of blowing agent from the inlet to the outlet.

17. The system of claim 16, wherein the control system sends an output to control the configuration of the bypass valve.

18. The system of claim 1, wherein the control system is designed to receive an input from an operator.

19. The system of claim 18, wherein the input from the operator activates the control system to enable the control system to send an output to the extruder to control pressure of polymeric material within the barrel.

20. The system of claim 18, wherein the supercritical fluid additive system includes an injector valve positioned between the inlet and the outlet, the injector valve having a first configuration which permits flow of blowing agent therethrough and a second configuration which prevents the flow of blowing agent therethrough, the input from the operator activating the control system to enable the control system to send an output to control the configuration of the injector valve.

21. The system of claim 18, wherein the operator provides an input to a first controller associated with the extruder, the first controller sending an output based on the input provided by the operator to a second controller associated with the supercritical fluid additive introduction system.

22. The system of claim 18, wherein the operator provides an input to a first controller associated with the supercritical fluid additive introduction system, the first controller sending an output based on the input provided by the operator to a second controller associated with extruder.

23. The system of claim 1, wherein the supercritical fluid additive system includes an injector valve positioned between the inlet and the outlet, the injector valve having a first

configuration which permits flow of blowing agent therethrough and a second configuration which prevents the flow of blowing agent therethrough.

24. The system of claim 23, wherein the control system is designed to receive an input indicative of the configuration of the injector valve.

25. The system of claim 23, wherein the control system is designed to send an output to control the configuration of the injector valve.

26. The system of claim 1, wherein the control system is designed to receive an input indicative of the pressure of polymeric material within the barrel.

27. The system of claim 26, wherein the control system is designed to provide indication to an operator when the pressure of polymeric material within the barrel is greater or less, by an offset value, than a desired pressure.

28. The system of claim 27, wherein the offset value is ± 200 psi.

29. The system of claim 26, wherein the polymeric material processing system is an injection molding system designed to operate in a series of molding cycles including a first molding cycle followed by a second molding cycle, the control system being designed to provide indication to an operator when the pressure of polymeric material within the barrel in the second cycle is greater or less, by an offset value, than the pressure of polymeric material within the barrel in the first molding cycle.

30. The system of claim 26, wherein the control system is designed to receive an input indicative of the pressure of polymeric material accumulated in a region within the barrel downstream of the screw.

31. The system of claim 1, wherein the control system is designed to send an output to the extruder to control the pressure of polymeric material within the barrel.

32. The system of claim 31, wherein the control system is designed to send an output to the extruder to control the pressure of polymeric material accumulated in a region within the barrel downstream of the screw.

33. The system of claim 1, wherein the control system is designed to receive an input indicative of the mass of supercritical fluid additive introduced into the polymeric material within the barrel.

34. The system of claim 33, wherein the control system is designed to provide indication to an operator when the mass of supercritical fluid additive introduced into the polymeric material within the barrel is greater or less, by an offset value, than a desired mass.

35. The system of claim 34, wherein the offset value is ±10mg of the desired mass.

36. The system of claim 34, wherein the polymeric material processing system is an injection molding system designed to operate in a series of molding cycles including a first molding cycle followed by a second molding cycle, the control system being designed to provide indication to an operator when the mass of supercritical fluid additive introduced into the polymeric material is greater or less, by an offset value, than the mass of supercritical fluid additive introduced into the polymeric material in the first molding cycle.

37. The system of claim 1, wherein the control system is designed to send an output to the supercritical fluid additive introduction system to control the mass of supercritical fluid additive introduced into the polymeric material.

38. The system of claim 1, wherein the control system is designed to receive an input indicative of the delivery pressure of supercritical fluid additive introduced into the polymeric material within the barrel.

39. The system of claim 38, wherein the control system is designed to provide indication to an operator when the delivery pressure of supercritical fluid additive introduced into the polymeric material within the barrel is greater or less, by an offset value, than a desired delivery pressure.

40. The system of claim 39, wherein the offset value is ± 50 psi.

41. The system of claim 39, wherein the polymeric material processing system is an injection molding system designed to operate in a series of molding cycles including a first molding cycle followed by a second molding cycle, the control system being designed to provide indication to an operator when the delivery pressure of supercritical fluid additive introduced into the polymeric material within the barrel in the second cycle is greater or less, by an offset value, than the delivery pressure of supercritical fluid additive introduced into the polymeric material within the barrel in the first molding cycle.

42. The system of claim 1, wherein the control system is designed to send an output to the extruder to control the delivery pressure of supercritical fluid additive introduced into the polymeric material.

43. The system of claim 1, wherein the control system includes a first controller associated with the extruder and a second controller associated with the supercritical fluid additive introduction system, the second controller sending an output to the supercritical fluid additive introduction system to not introduce supercritical fluid additive into polymeric material within the barrel in response to an input.

44. The system of claim 1, wherein the control system is designed to receive an input indicative of the rotational speed of the screw.

45. The system of claim 1, wherein the control system is designed to send an output to control the rotational speed of the screw.

46. The system of claim 4, wherein the control system is designed to receive an input from the mold.

47. A system for injection molding polymeric material comprising:

an extruder including a screw rotatable within a barrel to convey polymeric material in the direction of an outlet of the extruder, the barrel having a port formed therein connectable to a source of supercritical fluid additive; and

a clamping device constructed and arranged to clamp a mold defining a cavity connectable to the outlet of the extruder, the clamping device capable of providing a maximum clamping force of no greater than about 80% the minimum clamping force necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

48. The system of claim 47, wherein the clamping device is capable of providing a maximum clamping force of no greater than about 65% the minimum clamping force necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

49. The system of claim 47, wherein the clamping device is capable of providing a maximum clamping force of no greater than about 50% the minimum clamping force necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

50. The system of claim 47, wherein the clamping device is capable of providing a maximum clamping force of no greater than about 30% the minimum clamping force necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

51. The system of claim 47, wherein the clamping device is capable of providing a maximum clamping force of no greater than about 10% the minimum clamping force necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

52. The system of claim 47, wherein the supercritical fluid additive comprises carbon dioxide.

53. The system of claim 47, wherein the supercritical fluid additive consists essentially of carbon dioxide.

54. The system of claim 47, wherein the supercritical fluid additive comprises nitrogen.

55. The system of claim 47, wherein the supercritical fluid additive consists essentially of nitrogen.

56. The system of claim 47, wherein the system is constructed and arranged to form a polymeric foam article.

57. The system of claim 47, wherein the system is constructed and arranged to form a microcellular material article.

58. The system of claim 57, wherein the microcellular material article has an average cell size of less than about 100 microns.

59. The system of claim 47, wherein walls of the mold have a thickness no less than about 10% thinner than mold walls necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

60. The system of claim 47, wherein walls of the mold have a thickness no less than about 20% thinner than mold walls necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

61. The system of claim 47, wherein the mold comprises aluminum.

62. The system of claim 47, wherein the screw is axially reciprocatable within the barrel from a first position to a second position.

63. The system of claim 62, further comprising an injection device constructed and arranged to move the screw in an axial direction from the first position to the second position within the barrel to inject a mixture of polymeric material and supercritical fluid additive into the cavity, the injection device capable of providing an injection pressure of no greater than about 80% the injection pressure necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

64. The system of claim 63, wherein the injection device is capable of providing an injection pressure of no greater than about 65% the injection pressure necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

65. The system of claim 64, wherein the injection device is capable of providing an injection pressure of no greater than about 50% the injection pressure necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

66. The system of claim 47, further comprising a mold that includes a first mold half and a second mold half held together by the clamping force.

67. The system of claim 66, further comprising a first platen and a second platen, the first mold half being attachable to the first platen and the second mold half being attachable to a second platen, wherein at least one of the first and the second platens have a work surface area at least 10% greater than the work surface area of a platen usable to form an article from polymeric material free of a supercritical fluid additive within the cavity clamped with the clamping force.

68. A system for injection molding polymeric material comprising:

an extruder including a screw rotatable within a barrel to convey polymeric material in the direction of an outlet of the extruder, the barrel having a port formed therein connectable to a source of supercritical fluid additive;

a mold including a surface that defines, in part, a cavity connected to the outlet of the extruder, the mold surface that defines, in part, the cavity having a mold surface area; and

a clamping device constructed and arranged to clamp the mold with a clamping force necessary to form a molded article,

wherein the ratio of the clamping force to the mold surface area is less than about 1500 lbs/in^2.

69. The system of claim 68, wherein the ratio of the clamping force to the mold surface area is less than about 1000 lbs/in^2.

70. The system of claim 69, wherein the ratio of the clamping force to the mold surface area is less than about 750 lbs/in^2.

71. The system of claim 70, wherein the ratio of the clamping force to the mold surface area is less than about 500 lbs/in^2.

72. The system of claim 68, wherein the supercritical fluid additive comprises carbon dioxide.

73. The system of claim 68, wherein the supercritical fluid additive consists essentially of carbon dioxide.

74. The system of claim 68, wherein the source of supercritical fluid additive comprises nitrogen.

75. The system of claim 68, wherein the supercritical fluid additive consists essentially of nitrogen.

76. The system of claim 68, wherein the system is constructed and arranged to form a polymeric foam article.

77. The system of claim 76, wherein the system is constructed and arranged to form a microcellular material article.

78. The system of claim 77, wherein the microcellular material article has an average cell size of less than about 100 microns.

79. The system of claim 68, wherein the screw is axially reciprocatable within the barrel from a first position to a second position.

80. The system of claim 79, further comprising an injection device constructed and arranged to move the screw in an axial direction from the first position to the second position within the barrel to inject a mixture of polymeric material and supercritical fluid additive into the cavity, the injection device capable of providing an injection pressure of no greater than about 80% the injection pressure necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

81. The system of claim 80, wherein the injection device is capable of providing an injection pressure of no greater than about 50% the injection pressure necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

82. The system of claim 81, wherein the injection device is capable of providing an injection pressure of no greater than about 10% the injection pressure necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

83. The system of claim 68, wherein walls of the first and second mold halves have a thickness no less than about 10% thinner than mold walls necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

84. The system of claim 83, wherein walls of the first and second mold halves have a thickness no less than about 20% thinner than mold walls necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

85. The system of claim 68, wherein the first and second mold halves comprise aluminum.

86. A system for injection molding polymeric material comprising:

an extruder including a screw rotatable within a barrel to convey polymeric material in the direction of an outlet of the extruder, the barrel having a port formed therein connectable to a source of supercritical fluid additive; and

a clamping device constructed and arranged to clamp a first mold half and a second mold half together with a clamping force, the first and second mold halves, when clamped together, defining a cavity connected to the outlet of the extruder;

a first platen attachable to the first mold half; and

a second platen attachable to the second mold half,

wherein the first and the second platens have a work surface area at least 10% greater than the work surface area of platens usable to form an article from polymeric material free of a supercritical fluid additive within the cavity clamped with the clamping force.

87. The system of claim 86, wherein the first platen is fixed.

88. The system of claim 86, wherein the second platen is movable.

89. The system of claim 86, wherein first and the second platens have a work surface area at least 30% greater than the work surface area of platens usable to form an article from polymeric material free of a supercritical fluid additive within the cavity clamped with the clamping force.

90. The system of claim 86, wherein first and the second platens have a work surface area at least 50% greater than the work surface area of platens usable to form an article from polymeric material free of a supercritical fluid additive within the cavity clamped with the clamping force.

91. A system for injection molding polymeric material comprising:

an extruder including a screw rotatable within a barrel to convey polymeric material in the direction of an outlet of the extruder, the barrel having a port formed therein connectable to a source of supercritical fluid additive; and

an injection device constructed and arranged to move the screw in an axial direction within the barrel to inject a mixture of polymeric material and supercritical fluid additive into a cavity of a mold connected to the outlet of the extruder, the injection device capable of providing an injection pressure of no greater than about 80% the injection pressure necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

92. The system of claim 91, wherein the injection device is capable of providing an injection pressure of no greater than about 65% the injection pressure necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

93. The system of claim 91, wherein the injection device is capable of providing an injection pressure of no greater than about 50% the injection pressure necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

94. The system of claim 91, wherein the system is constructed and arranged to form a polymeric foam article.

95. The system of claim 94, wherein the system is constructed and arranged to form a microcellular material article.

96. The system of claim 94, further comprising a clamping device constructed and arranged to clamp the mold, the clamping device capable of providing a maximum clamping force of no greater than about 80% the minimum clamping force necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

97. The system of claim 96, wherein the clamping device is capable of providing a maximum clamping force of no greater than about 50% the minimum clamping force

necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

98. The system of claim 97, wherein the clamping device is capable of providing a maximum clamping force of no greater than about 10% the minimum clamping force necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

99. A system for injection molding polymeric material comprising:

an extruder including a screw rotatable within a barrel to convey polymeric material in the direction of an outlet of the extruder, the barrel having a port formed therein connectable to a source of supercritical fluid additive;

an injection device constructed and arranged to move the screw in an axial direction within the barrel to inject a mixture of polymeric material and supercritical fluid additive into a cavity of a mold connected to the outlet of the extruder, the injection device capable of providing an injection pressure of no greater than about 80% the injection pressure necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity; and

a clamping device constructed and arranged to clamp the mold, the clamping device capable of providing a maximum clamping force of no greater than about 80% the minimum clamping force necessary to form an article from polymeric material free of a supercritical fluid additive within the cavity.

100. A system for processing polymeric material comprising:

an extruder including a screw rotatable within a barrel to convey polymeric material in the direction of an outlet of the extruder, the barrel having a port formed therein; and

a supercritical fluid additive introduction system having an inlet connectable to a supercritical fluid additive source and an outlet connectable to the port, the introduction system being directly mounted to the system.

101. The system of claim 100, wherein the introduction system is directly mounted to a frame of the extruder.

102. The system of claim 100, wherein the introduction system comprises a metering device.

103. The system of claim 100, wherein the supercritical fluid additive source is separate from the extruder.

104. The system of claim 100, further comprising a mold defining a cavity connected to the outlet of the extruder.

105. A method for forming a molded article comprising:

providing a polymeric material molding system including an extruder and a mold, the system constructed and arranged to deliver polymeric material free of supercritical fluid additive from the extruder into the mold and forming an injection molded article using a first minimum clamping force; and

delivering polymeric material admixed with a supercritical fluid additive from the extruder into the mold, and forming the injection molded article using a second minimum clamping force less than about 80% the first minimum clamping force.

106. A method for forming a molded article comprising:

introducing a polymeric material and supercritical fluid additive mixture into a mold;

clamping the mold with a clamping force of less than about 80% of the minimum clamping force required to form a molded article from the polymeric material free of the supercritical fluid additive; and

forming a molded article.

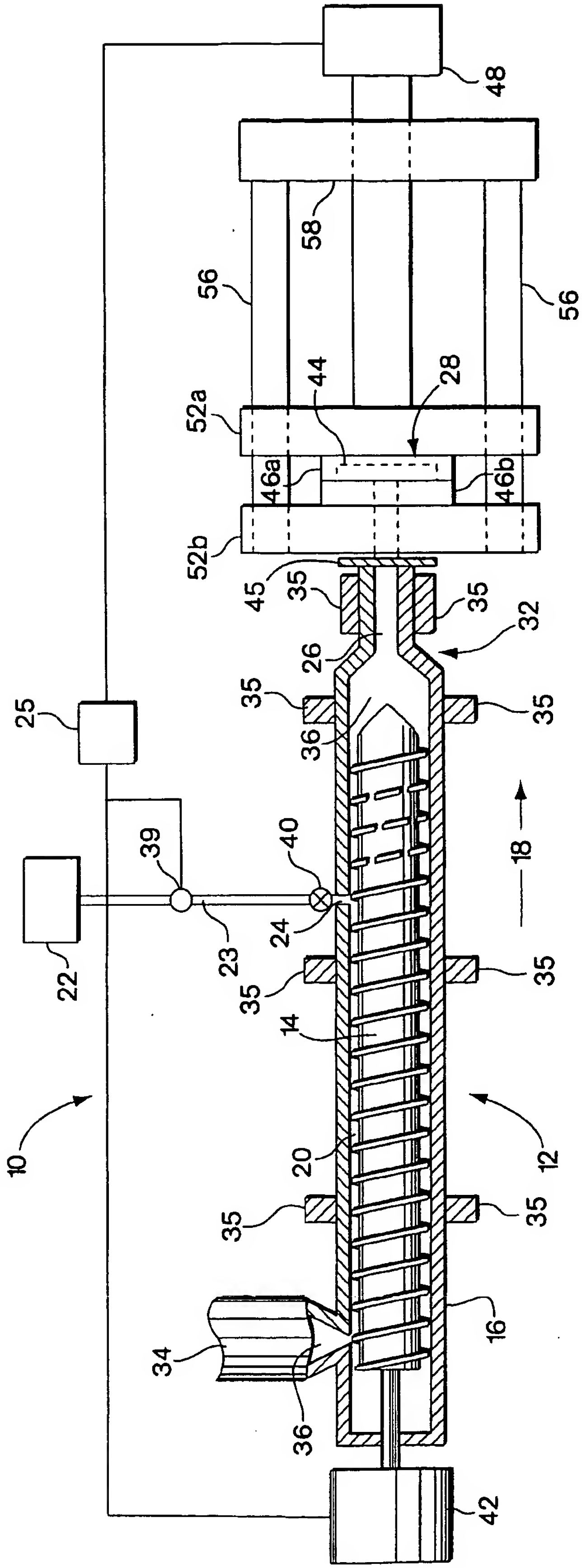
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Fig. 1A

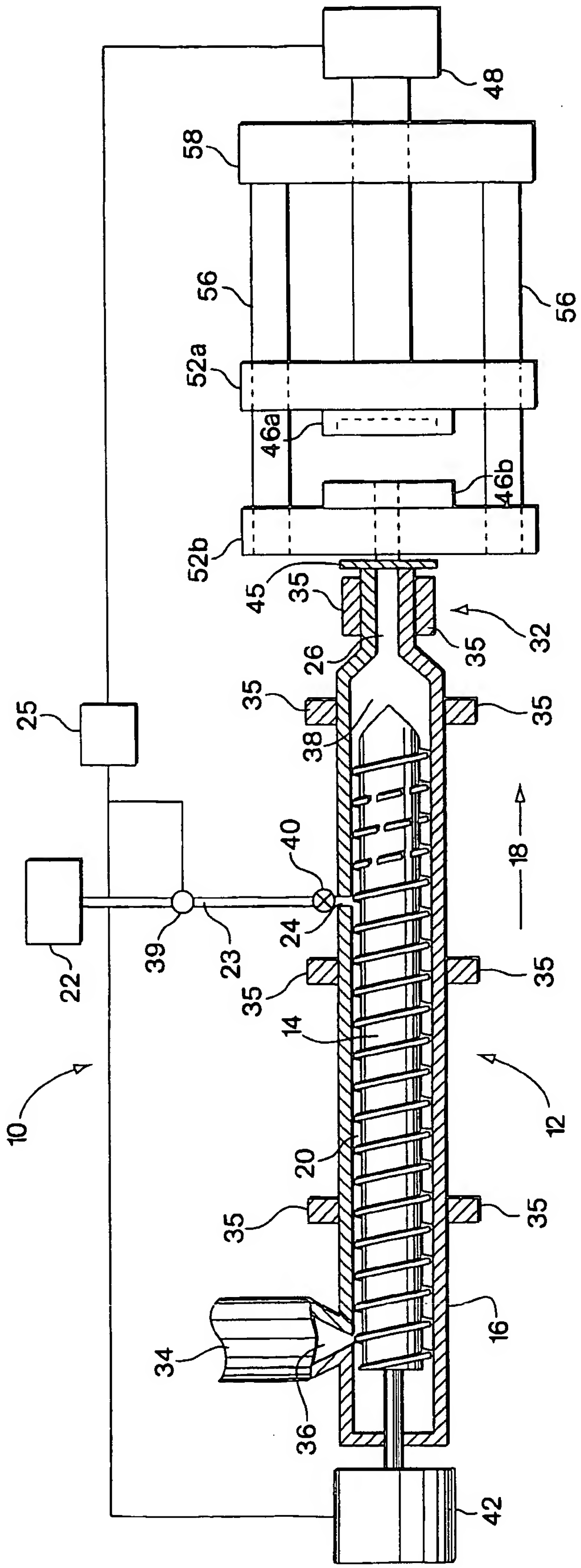
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Fig. 1B

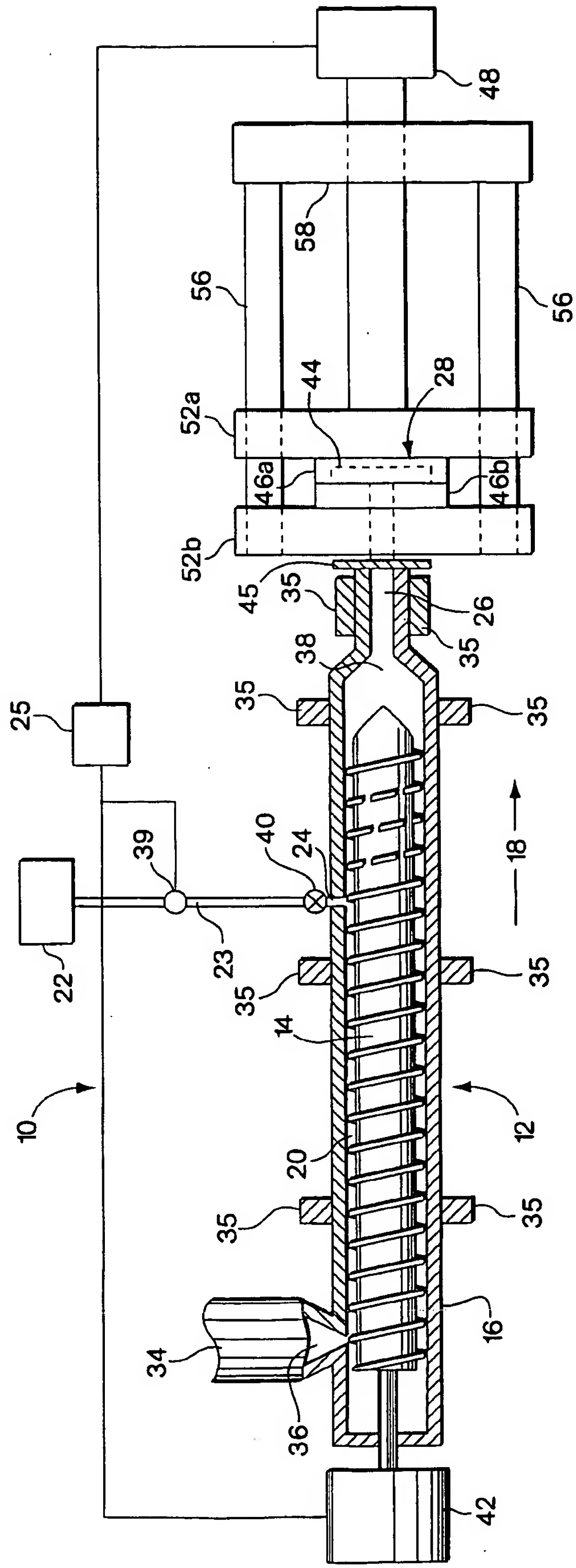
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Fig. 1C

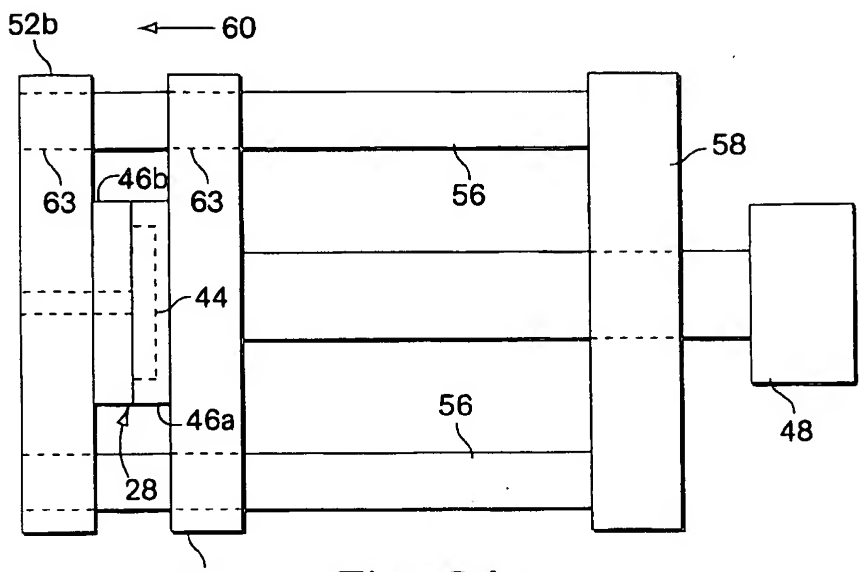
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Fig. 2A

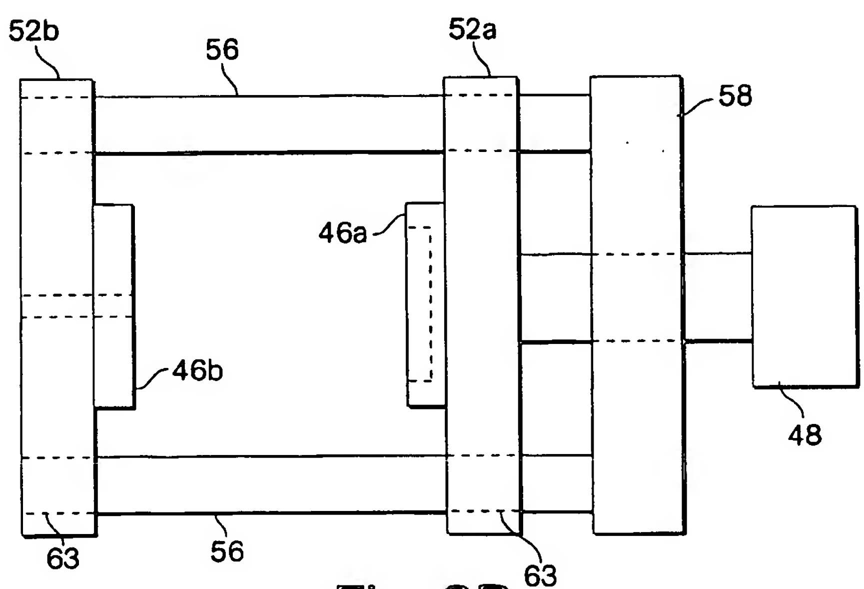
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Fig. 2B

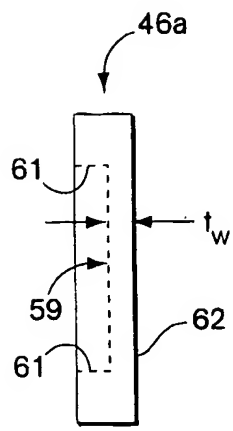

Fig. 3

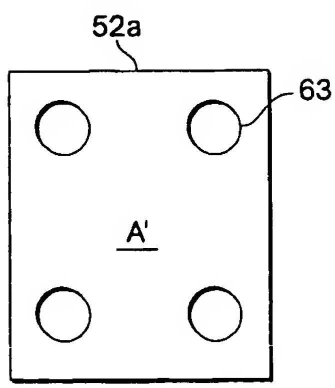

Fig. 4A

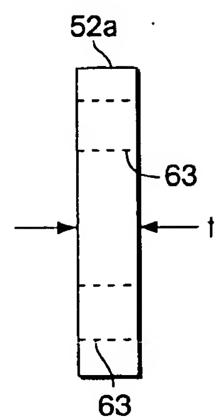

Fig. 4B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US02/14154

A. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
Name and mailing address of the ISA/ Facsimile No.	Authorized officer Telephone No.

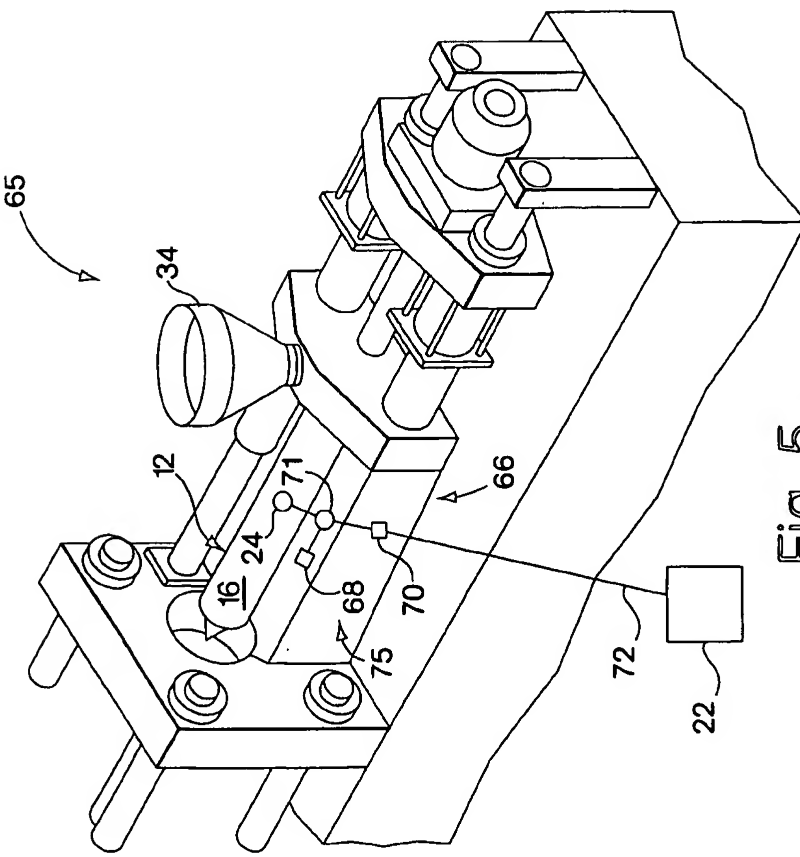

Fig. 5